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METAL MATRIX COMPOSITES (GRAPHITE-ALUMINUM WIRE) PHASE I.(U)
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REPORT NO. MT-044
APRIL 1977

METAL MATRIX COMPOSITES

(GRAPHITE - ALUMINUM WIRE)

PHASE 1

A PROJECT OF THE
MANUFACTURING TECHNOLOGY PROGRAM
NAVAL SEA SYSTEMS COMMAND

FINAL REPORT

NAVAL ORDNANCE STATION
LOUISVILLE, KENTUCKY 40214

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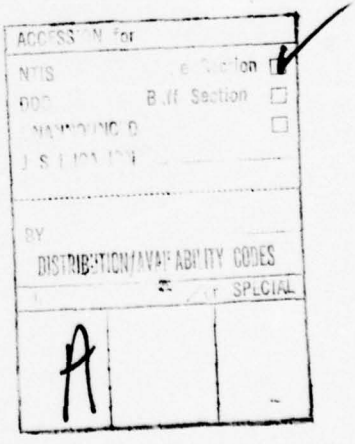
ABSTRACT

The objectives of the program were to 1) develop a production process to produce rayon precursor graphite-aluminum wire with a capacity of 1000 lbs per year in accordance with Naval Sea Systems Command development specification for metal-matrix composites MTP-114, dated 13 January 1975; 2) optimize the process for the design of a single unit that would produce 2000 lbs of polyacrylonitrile (PAN) graphite-aluminum wire per year; and 3) demonstrate the 1000 lb per year production process by producing 100 lbs of graphite-aluminum wire.

Task I involved the design of the 1000 lb/year unit and included studies to refine techniques for operations such as open melt processing, open yarn feed-in to the titanium/boron (Ti/B) coating unit, polyvinyl alcohol (PVA) yarn sizing removal and chemical vapor deposition (CVD).

Task II primarily consisted of optimizing the 1000 lb/year unit including system refinements and wire property testing to prepare the equipment for production capability. Data obtained from these studies were coupled with recent developments in the PAN graphite-aluminum area leading to a conceptual design of a single unit with a 2000 lb/year capacity.

Task III demonstrated the capability of the 1000 lb/year unit with the production and delivery of 100 lbs of 201 aluminum alloy T50 graphite wire by continuous processing commensurate with a 50% yield factor. Careful system monitoring and proper mechanical testing demonstrated that the wire produced exceeded the 90% rule of mixture (ROM) requirement.



FOREWORD

This final technical report summarizes the work performed under NAVSEASYSCOM Request No. N00024-75-RC-5838R issued to develop a 1000 pound per year capability for the production of graphite-aluminum wire. The program was divided into four tasks; I) production process development for 1000 lb./year capacity unit, II) process optimization study leading to the development of a 2000 lb./year PAN graphite-aluminum unit, III) production and delivery of 100 lbs. of graphite-aluminum wire, and IV) reporting. Fiber Materials, Inc. conducted the design and engineering studies for both the 1000 and 2000 lb./year units and Material Concepts, Inc. conducted the process optimization studies and manufactured 100 lbs. of graphite-aluminum wire to demonstrate the 1000 lb./year production unit.

This report was prepared by Fiber Materials, Inc. and has been edited by Naval Ordnance Station, Louisville to insure compliance with the total requirements of the NAVORDSYSCOM work statement.

Funding was provided by the Manufacturing Technology Branch, SEA-0354, Naval Sea Systems Command.

This Manufacturing Technology report has been reviewed and is approved.

Thad Peake

THAD PEAKE
Director, Manufacturing
Technology Department
Naval Ordnance Station
Louisville, Kentucky

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TABLE OF CONTENTS

TABLE OF CONTENTS (Continued)

TABLE OF CONTENTS (Continued)

TABLE OF CONTENTS (Continued)

LIST OF ILLUSTRATIONS

LIST OF TABLES

LIST OF ABBREVIATIONS

Term	Abbreviation
Pound	lb.
Rule-of-mixtures	ROM
Polyvinyl alcohol	PVA
Chemical vapor deposition	CVD
Titanium	Ti
Boron	B
Titanium tetrachloride	$TiCl_4$
Boron trichloride	BCl_3
Polyacrylonitrile	PAN
Giganewton force per square meter	GPa
Meganewton force per square meter	MPa
1000 pounds force per square inch	ksi
Pounds force per square inch	psi
One million pounds force per square inch	msi
Volume percent	v/o
Silicon carbide	SiC
Nitrogen	N_2
Argon	Ar
Hydrogen	H_2
Zinc	Zn
Hydrochloric acid	HCl
Nitric acid	HNO_3
Linear weight	g/cm
Ultimate tensile strength	UTS
Graphite Aluminum	Gr/Al

SECTION 1

INTRODUCTION

Graphite-aluminum composites offer the potential for weight saving structural materials to be used in a wide range of Navy applications. Metal-matrix composites exhibit high specific strength and specific modulus over a wide temperature range for use in, for example, RV substructures, truss members, stiffeners, pressure vessels, radar masts, and internal structural members of hydrofoils. Graphite-aluminum composites also enjoy property advantages over present organic composites in temperature capabilities, shear strength, compressive strength and design flexibility in joining.

Carbon and graphite fibers have always shown great potential as reinforcement in metal-matrix composites because of their high strength and stiffness, low density, and predicted large-scale production at low cost. The development of premium high strength and stiffness rayon precursor graphite fibers over the last ten years surpasses the developments of conventional metals in terms of potential improvements in strength and particularly in the stiffness of structural materials. For example, rayon precursor fibers with a strength of 300,000 Psi (2070 MPa) and a modulus of elasticity of 55×10^6 Psi (380 GPa) are commercially available at the present time.

More recently, technology has been developed for the production of graphite fibers from low-cost pitch and, it is now anticipated that, within the next five years, performance equal to that achieved with rayon precursor graphite fibers will be realized. Union Carbide Corporation is currently considering a pilot production plant for pitch precursor graphite fibers. The development of these fibers will have a tremendous impact on the industry since it will facilitate the production of lightweight graphite composites of substantially increased strength and stiffness at lower costs.

High performance polyacrylonitrile (PAN) precursor graphite fibers of moderate cost have also been available for the past several years and are used widely to reinforce plastic matrices. Strengths in excess of 400,000 Psi (2760 MPa) at $30\text{-}50 \times 10^6$ Psi modulus (207-345 GPa) are typical mechanical properties of these fibers.

The most significant achievement in the graphite-aluminum composite area has been the development of the liquid infiltration process for impregnating graphite fiber yarns with molten metals and their alloys (1)(2). The process involves the deposition of very small concentrations of titanium and boron to promote the wetting of graphite fibers by aluminum alloys. A scanning electron

micrograph of a fracture end of a Thornel 50 graphite-aluminum alloy wire is shown in Figure 1, demonstrating the excellent wetting characteristics and fiber distribution obtained using this process.

Fiber Materials, Inc. and the Aerospace Corporation have conducted extensive testing on graphite-aluminum composite material produced by this method. Tensile and creep tests at temperatures up to 1000°F have suggested that a graphite-aluminum system is stable at missile substructure temperatures. Other significant work at Aerospace has shown graphite-aluminum to have good fatigue resistance, resistance to degradation on thermal cycling, high dimensional stability, and good wear properties. Table 1 shows typical mechanical properties of T50 graphite-aluminum composite wire and fabricated test bars.

This program was devoted toward process improvement of existing pilot plant units to produce graphite-aluminum wire preform material at a 1000 lb./year capacity. To scale-up the infiltration unit into a manufacturing process, it was necessary to determine limiting factors controlling the maximum output speed. It also became evident during early studies that research style equipment would have to be replaced by more production oriented units if a true manufacturing plant were to evolve.

During Task I, critical areas thought to be capacity limiting were examined, designs were evaluated, and changes were made to assure that the most efficient process was adopted for the final unit. For example, graphite yarn feed-in boxes and closed melt retorts were replaced with open yarn reels and foundry style open melts for easier fiber handling. These and other process parameters were investigated during this task.

Task II originally called for optimization studies leading to the design of a single unit that would produce 5000 lbs. of rayon precursor graphite-aluminum wire per year.

Prior to FY 1976, rayon based graphite fibers were used almost exclusively in the development of metal-matrix composites. Rule-of-mixture tensile and modulus mechanical properties have been attained utilizing a variety of aluminum alloys with Union Carbide's high modulus T50 fibers. Rayon fibers were therefore chosen for the manufacturing scale-up program.

Previous work using PAN based fibers in metal matrices indicated that PAN based graphite was more reactive with the aluminum than was the rayon based graphite and, therefore, less able to transfer its excellent strength into a composite (Table 2). During the past year, a significant breakthrough was made at FMI in research and development on PAN graphite fiber reinforced aluminum. New fiber barrier coatings were developed and demonstrated which prevented attack and degradation of the fibers by the

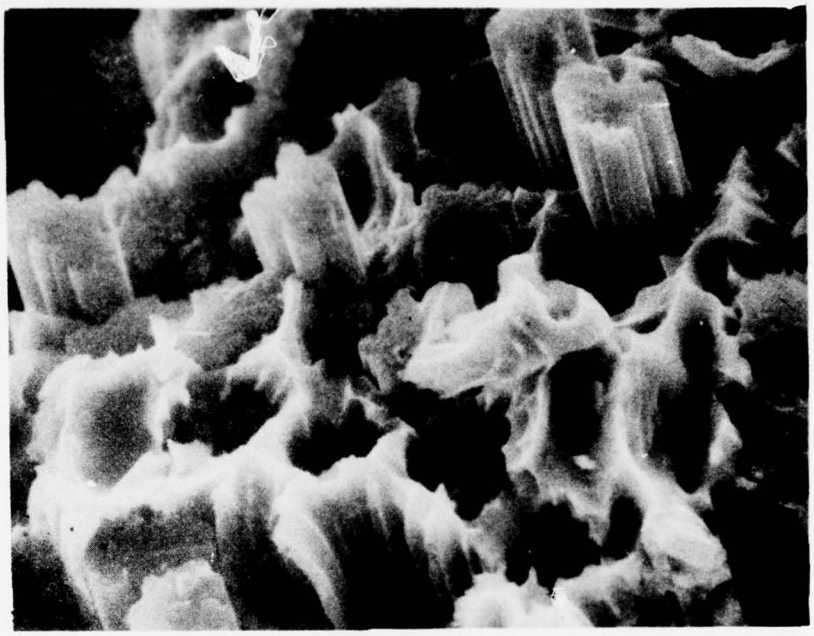


FIGURE 1 T50 (RAYON BASED) A201 TENSILE FRACTURE

Property	28 v/o T50[(1)]/A201 Wire	35 v/o T50/A201 Wire	42 v/o T50/A201 Wire	30 v/o T50/A201 Test Bar
Tensile strength	100 ksi 690 MPa	120 ksi 828 MPa	155 ksi 1069 MPa	90 ksi 621 MPa
Tensile modulus	21 msi 152 GPa	27 msi 193 GPa	30 msi 207 GPa	20 msi 138 GPa
Transverse strength	5 ksi 34.5 MPa	5 ksi 34.5 MPa	---	7.1 ksi 49.0 MPa

(1) Union Carbide Corporation 50 million psi modulus rayon precursor fiber

TABLE 1 TYPICAL STATE-OF-THE-ART T50 GRAPHITE-ALUMINUM COMPOSITE MECHANICAL PROPERTIES

Property	As Received T300[1] A201 Alloy	Barrier Coated T300 A201 Alloy	As Received Modmor 1[2] A201 Alloy	Barrier Coated Modmor 1 A201 Alloy
Tensile strength	50.2 ksi 346.4 MPa	180 ksi 1242 MPa	59.0 ksi 407.0 MPa	133 ksi 918 MPa
Tensile modulus	---	20 msi 138 GPa	---	18.1 msi 1254 GPa
Fiber content	45.9%	40.0%	28%	30%

(1) Union Carbide Corporation 30 million modulus PAN precursor fiber

(2) Morganite Modmor, Inc. 50 million modulus PAN precursor fiber

MECHANICAL PROPERTY COMPARISON PAN BASED GRAPHITE-ALUMINUM COMPOSITES

TABLE 2 (PAST DATA VS. PRESENT STATE-OF-THE-ART)

aluminum matrix during liquid metal infiltration and subsequent fabrication of wire into shapes. Both high and moderate modulus PAN fibers have been processed with these new coatings. This achievement has led to a dramatic increase in the longitudinal and off-axis strength and ductility of graphite-aluminum and the use of low-cost fibers ($30 per lb.) with superior handling qualities to T50.

This breakthrough, coupled with the fact that rayon based graphite fibers have steadily increased in price and the future supply of rayon fibers is questionable, prompted the sponsor to consider changing fiber precursors. Task II was consequently altered, and optimization studies were performed leading to the design of a single unit with the capacity to produce 2000 lbs. of PAN graphite-aluminum per year. It has also been proposed that PAN graphite or new pitch graphite be used in the scale-up program immediately following.

Task III demonstrated unit feasibility with the production of 100 lbs. of graphite-aluminum by continuous processing giving a greater than 50% yield factor. The wire consisted of A201 aluminum alloy and T50 graphite fibers. During the optimization studies on the 1000 lb./year unit, tensile testing, metallography, and chemical analyses were conducted on wire produced to identify the effects of various changes in process parameters on wire properties. Optimum operating conditions were established, and careful monitoring of these system variables assured the production of consistent wire above the 90% ROM mechanical property requirement.

This scale-up effort and future manufacturing scale-up programs will increase production capacity to one million pounds per year and will provide materials at costs well below $100 per pound.

SECTION 2

1000 LB. UNIT DESIGN STUDIES (TASK I)

2.1 GENERAL SCOPE

Design studies to develop a graphite-aluminum unit with a 1000 lb./year capacity were performed using the equipment shown in Figure 2. PVA removal and precoat furnaces were added to the process in the latter stages for fiber preconditioning and are represented schematically in Figure 3. Equipment used and their specifications are as follows:

	Zone	Temp. Capabilities
(1) PVA Burn-Off Furnace	2'	1000°C
(2) Precoat Furnace	2'	1200°C
(3) CVD Reaction Furnace	3'	1200°C
(4) Retort Furnace	12" deep 8" dia.	1200°C

Both the CVD reaction and precoat furnaces used were Lindberg tube types. The PVA burn-off and retort furnaces were fabricated at FMI to satisfy dimensional requirements during the program. Modifications were made on the existing graphite-aluminum infiltration unit during scale-up studies to improve both the quality and quantity of wire produced in any given period. Limitations of the present system were attacked by engineering study, and design changes were incorporated.

The following categories were identified early in the program to be major capacity limiting areas, and steps taken to solve these problems are included in the detailed scope section:

(1) Elimination of closed retort;
(2) Elimination of yarn box for fiber feed-in;
(3) Effects of various yarn sizing removal techniques;
(4) Effects of increased zone length in the reaction chamber;
(5) Effect of N_2 instead of the argon cover gas;
(6) Steps taken to facilitate fiber handling.

Subtle changes in operating parameters or process set-up often had pronounced effects on wetting by aluminum. Each parameter change was therefore evaluated, and its effect on wire properties was determined. In this manner, a manufacturing scale-up evolved with maximum efficiency and composite properties. The

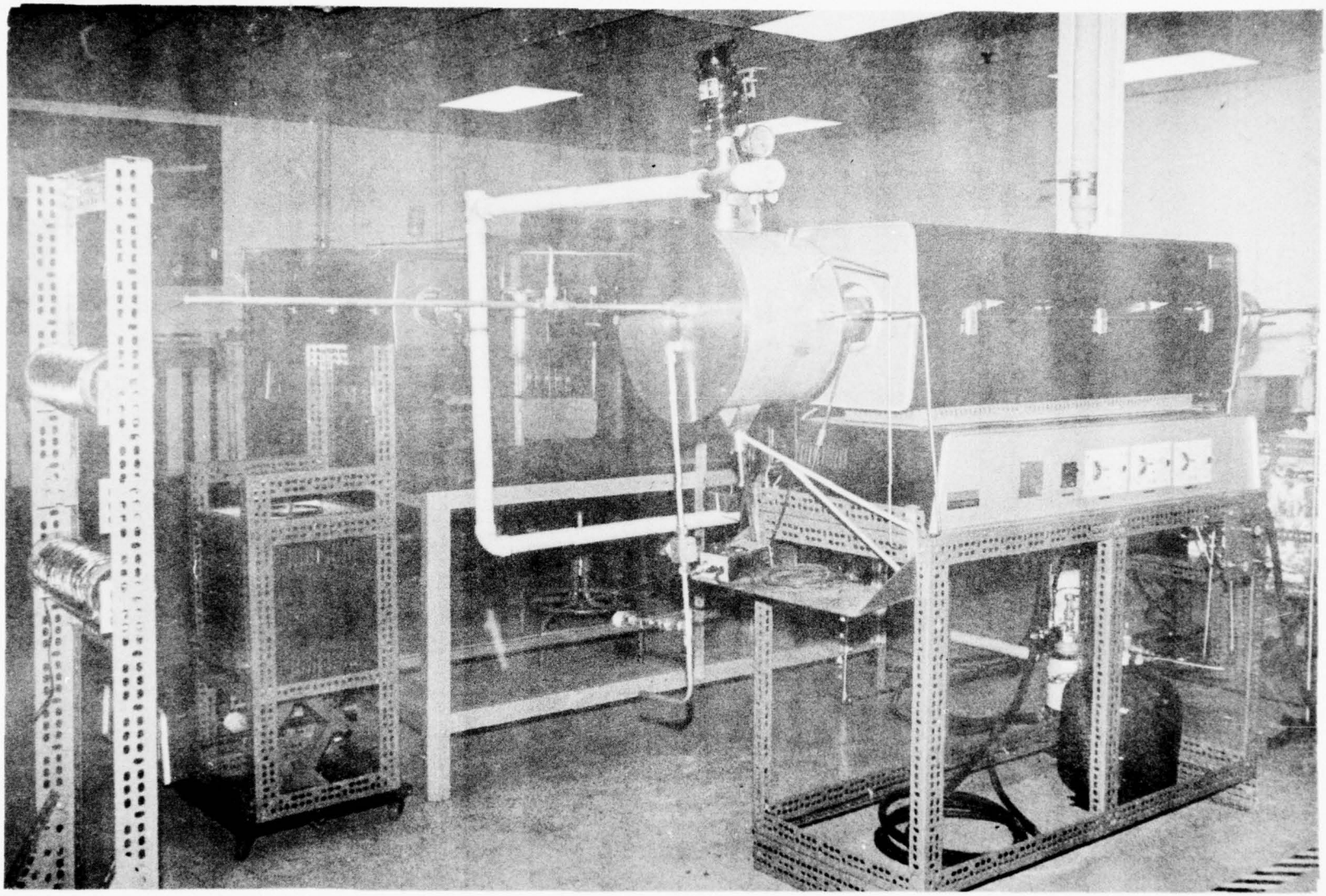


FIGURE 2 LABORATORY EQUIPMENT FOR DESIGN STUDY

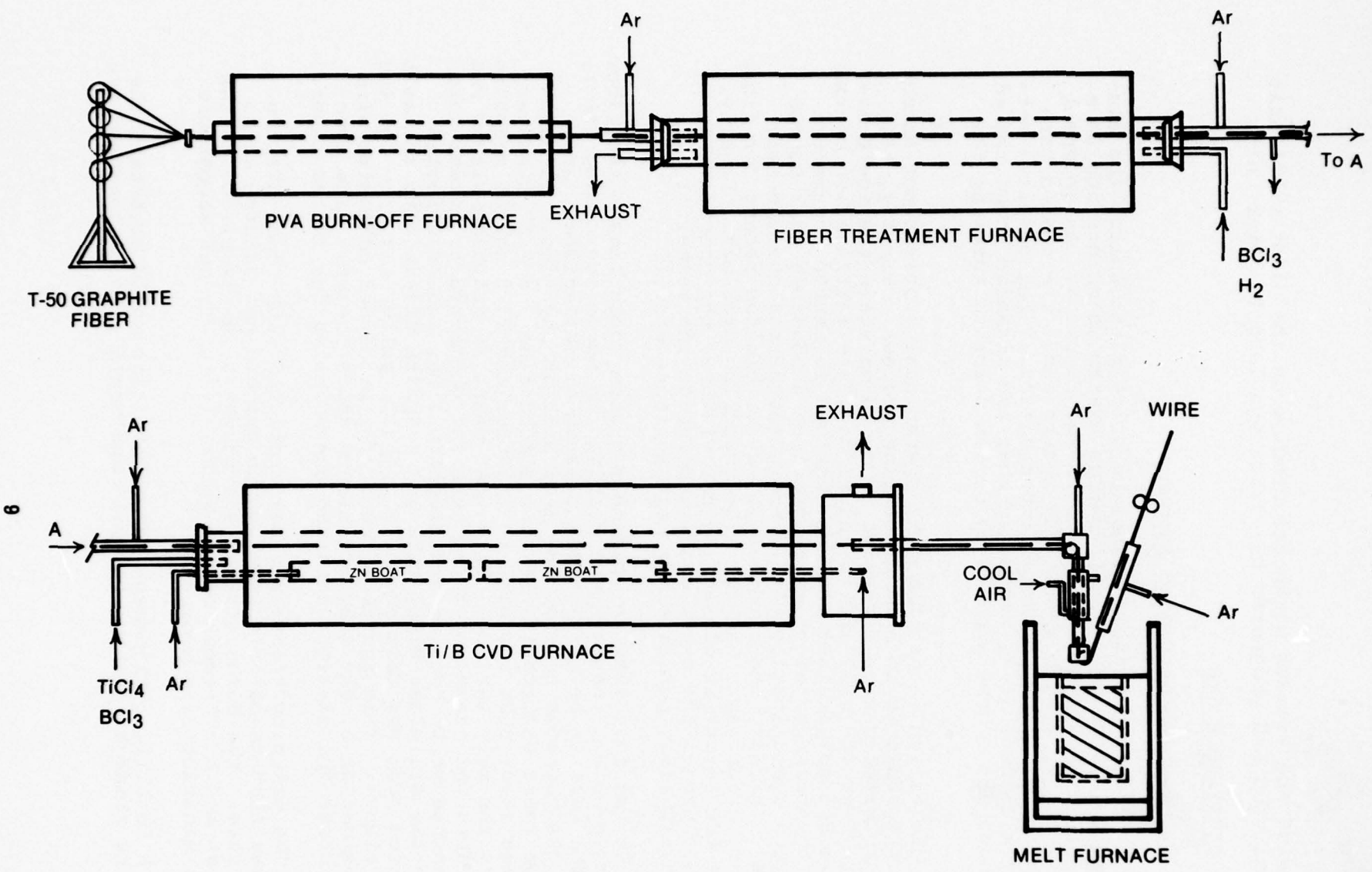


FIGURE 3 **EXPERIMENTAL SCALE-UP UNIT**

results of the various parameter studies on the pilot plant unit were analyzed and projected to design the 1000 lb./year unit.

2.2 DETAILED SCOPE

2.2.1 Elimination of Closed Retort

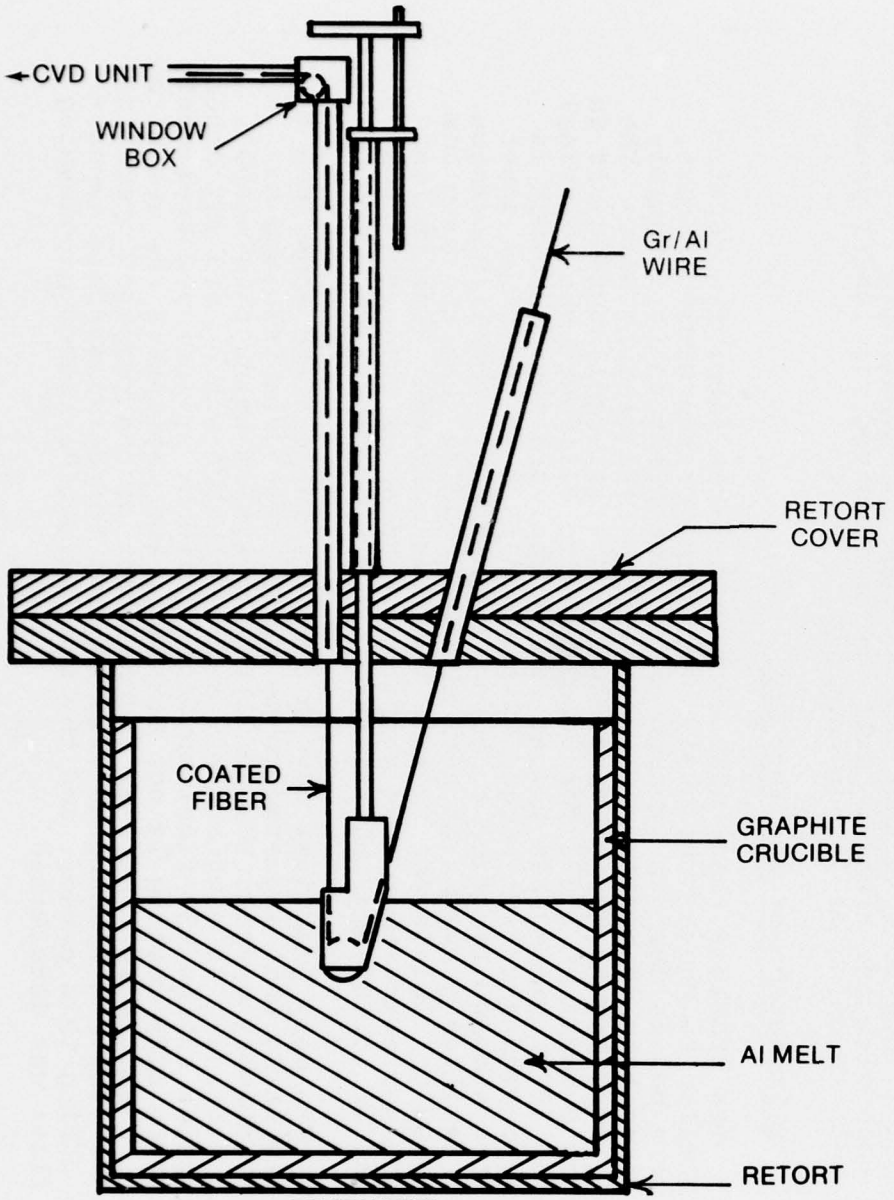
In existing graphite-aluminum pilot plant units, the aluminum melt in the liquid infiltration system is maintained in a closed retort under an inert atmosphere, Figure 4. An internal graphite pulley system within the retort feeds the coated yarn through the aluminum for metal impregnation. (For complete wetting by aluminum, it is necessary that the titanium boron coated fiber does not become exposed to oxygen prior to entering the melt.)

The closed retort has many operational problems not amenable toward scale-up in a manufacturing process. Firstly, the closed retort requires excessive argon to maintain the inert atmosphere over the melt and to insure complete infiltration of the fibers. Secondly, a hot seal is required to fasten the retort lid to the base container which provides a possible leak source for oxygen contamination within the atmosphere above the melt surface. Thirdly, the internal pulley within the retort for fiber transport often jams, causing fiber handling problems. Finally, because the retort is closed and not visible, the operator can never be sure of the exact condition inside the vessel (i.e., melt level, fiber positioning, melt surface, etc.).

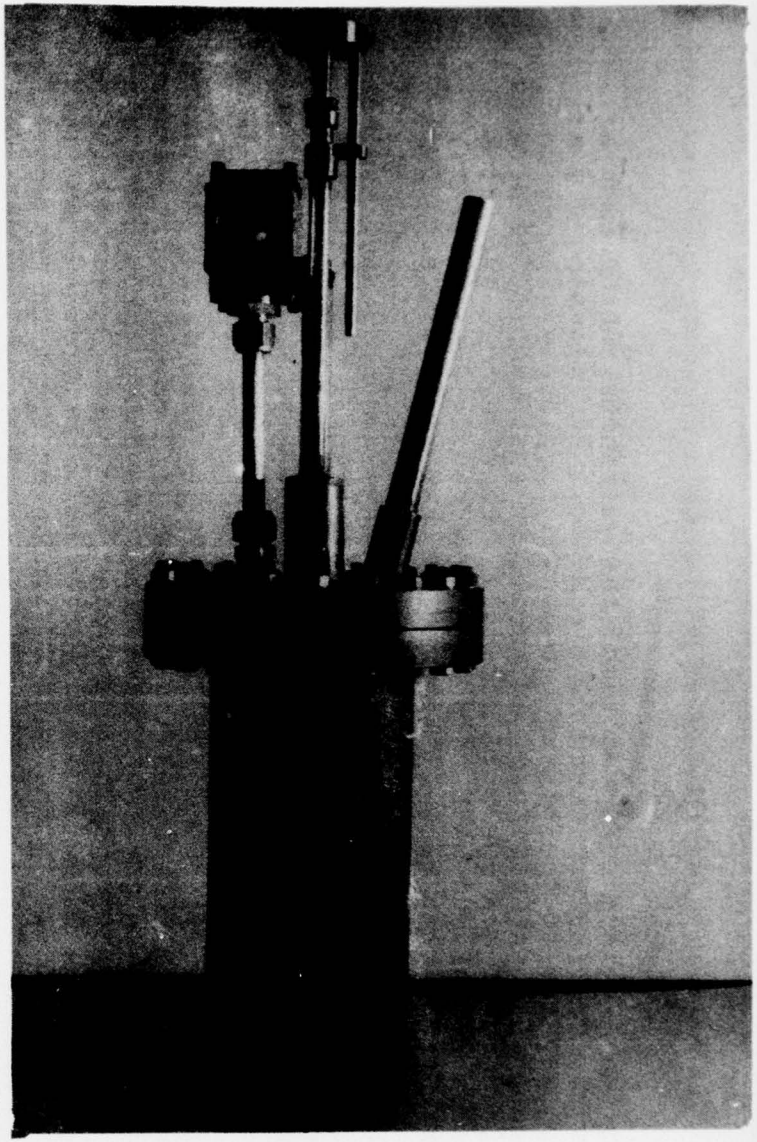
It was felt that an open melt system would lessen the fiber handling problem, reduce argon required to purge the coated fiber, allow the melt to be continually cleaned or replenished, and permit the operator to view the melt area at any time. To maintain the inert atmosphere near the coated fiber, a 1/2" diameter stainless steel tube was used to transfer the Ti/B coated graphite fiber to the melt surface. From that point, a graphite sleeve was fitted onto the stainless steel tube and permitted to extend into the aluminum melt. The coated graphite fiber was transported through the stainless steel tube and graphite sleeve into the melt and exited from the melt around a graphite pulley fixed to the end of the sleeve. This system successfully processed composite wire until oxidation of the graphite sleeve above the melt line eventually broke the airtight seal and contaminated the coated fiber.

The graphite sleeve was next replaced with boron nitride which was also compatible in aluminum but did not oxidize at so high a rate. The boron nitride was adequate; however, due to the high cost and brittleness of the material, it was not acceptable for the manufacturing process.

A metallic replacement was sought that would withstand the oxidizing atmosphere above the melt and would also be non-reactive



SCHEMATIC REPRESENTATION



PHOTOGRAPH

FIGURE 4 **CLOSED ALUMINUM RETORT DESIGN**

with molten aluminum. It was found that titanium tubing with a heavy oxide coating met these requirements. By fastening a graphite pulley arm to the titanium tube and completely submerging the graphite in the aluminum, an excellent seal was formed between the molten metal and the oxidized tube. Considerable operating experience was gained with this technique during design trials, and various refinements were made to further improve its performance. These changes are summarized in Table 3. In particular, it was found that increased infiltration speeds and graphite-aluminum wire quality could be obtained by cooling the oxidized titanium tube in a zone just above the melt line. The primary reason for improvement on cooling the tube was thought to be reduction in oxidation of the Ti/B coatings leading to more rapid fiber wetting.

The final system design, Figure 5, includes a 3/4" diameter oxidized titanium tube extending from the Ti/B coating unit window box into the aluminum. The coated fiber was drawn through the aluminum over a graphite pulley arm system completely submerged in the melt (no graphite oxidation) and exited as wire through a one inch diameter Ti (oxidized) tube purged with N_2 or argon to prevent oxide formation on its surface.

The present design has been successfully proven during production; however, further improvements in compatibility of the feed tube with the aluminum melt may be required for longer production runs in units of larger capacity.

2.2.2 Elimination of the Yarn Box

The problems that exist with a yarn box fiber feed system are similar to those previously mentioned for the closed retort. The yarn box is used in the research pilot plant units to supply the fiber into the coating chamber of the infiltrating unit. The supply of fiber is housed on a stainless steel reel, burned-off in a batch process at 350°C for 30 minutes to eliminate the polyvinyl alcohol (PVA) sizing and placed within the yarn box. The box is then vacuumed and back-purged with argon to keep the fiber under an inert atmosphere prior to being drawn through the Ti/B furnace. Fiber handling problems or reel changes require that the yarn box be opened to replace the fiber. Valuable operating time is lost in sealing, evacuating, and purging the yarn box prior to reconnecting it to the coating chamber.

The only practical way to feed the multistrand tows into a manufacturing unit appeared to be a direct feed-in from the air. To effectively operate the infiltration system using this method, it is necessary to continuously remove the PVA sizing and any other impurities on the T50 fiber surface. Without a fiber pre-treatment, a uniform Ti/B coating is not attained, and wetting of the graphite by the aluminum melt becomes inconsistent at the required operating speeds. Various techniques were studied to remove surface impurities during this period, and the most effective method of cleaning the fiber was determined.

Open Melt Arm Material	Pulley and Sleeve Material	Seal Placement Between Arm and Sleeve	Gas Exit Port	Cooling	Comments
1/2" stainless steel tube	Graphite	Above melt line	None	None	Infiltration 6-24 inches/minute; Graphite oxidized
1/2" stainless steel tube	SiC coated graphite	Above melt line	None	None	Better oxidation resistance
1/2" stainless steel tube	Boron nitride	Above melt line	None	None	Good seal, best oxidation resistance, BN expensive
1/2" titanium tube	Graphite	Below melt line	None	None	Good infiltration, excellent seal; Ti eventually dissolved in Al
1/2" titanium tube oxidized	Graphite	Below melt line	None	None	Less reaction of tube with aluminum
3/4" titanium tube oxidized	Graphite	Below melt line	None	None	No fiber rubbing
3/4" titanium tube oxidized	Graphite	Below melt line	1/4" welded tube near melt surface	None	Infiltration not so fast
3/4" titanium tube oxidized	Graphite	Below melt line	None	Co-current	Infiltration excellent at fastest speeds

TABLE 3 SUMMARY OF OPEN MELT ARM DEVELOPMENT

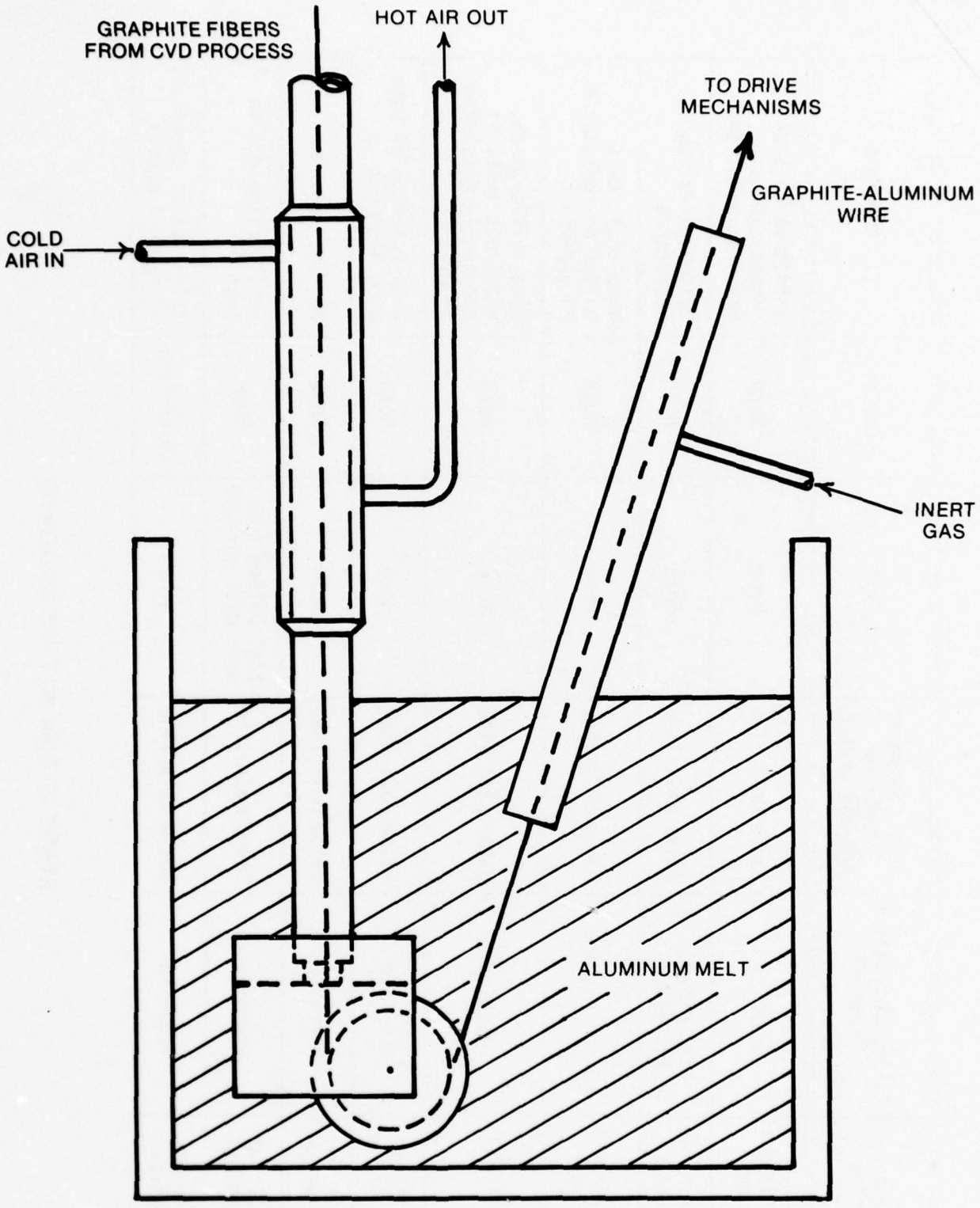


FIGURE 5 **OPEN MELT PULLEY ARM SET-UP**

2.2.2.1 Water Solubility Studies to Remove PVA

Polyvinyl alcohol is extremely soluble in hot water, and studies were performed to dissolve the PVA sizing from the fiber surface in boiling water containing small amounts of detergent.

A reel of eight strand Thornel 50 fiber was washed eight times in boiling water containing a trace of NaOH (as a wetting agent), rinsed in distilled water, and dried in an oven at 120°C for eight hours. A spot test for PVA showed no apparent sizing remained. Attempts were made to infiltrate this "water sized" fiber with little success, Table 4.

Evidently, non-detected traces of PVA and/or water molecules most likely absorbed or mechanically trapped within the fibers were present in a large enough quantity to inhibit the aluminum infiltration process. Further work in this area was terminated.

2.2.2.2 PVA Sizing Removal Using Burn-Off Treatment

Polyvinyl alcohol decomposes by thermal treatment above 150°C, releasing water and leaving a slight carbon residue. Since a batch process for removing PVA has been successfully used in the existing laboratory unit, an in-line burn-off furnace was positioned between the as-received fiber and the Ti/B CVD reaction chamber. A 24" bake-out furnace was used to investigate the thermal treatment effects on Thornel 50 fiber at temperatures between 150°C and 900°C under nitrogen, argon, and oxygen atmospheres. Within the burn-off temperature range of 150°C to 350°C, wire was produced at 18 to 24 inches per minute regardless of the atmosphere. Increases in temperature above 350°C did not improve wire speeds and, in fact, had adverse effects on the infiltration process, Table 5.

2.2.2.3 PVA Sizing Removal Using Chemical Treatment

Infiltration studies were performed to determine the effects of chemical pre-treatment of the sized yarn to remove impurities from the fiber surface prior to entering the Ti/B reaction chamber. The tows were chemically treated with boron trichloride and/or titanium tetrachloride, using either inert atmospheres or reducing atmospheres. Temperatures between 300°C and 1000°C were investigated, and a 24" heating zone was used throughout the trials.

The effects of boron trichloride in a hydrogen reducing atmosphere were most pronounced in improving both the speed and quality of the graphite-aluminum wire. Composite wire at 40 inches per minute was obtained by pre-treating the fiber surface in this way prior to the Ti/B reaction, Table 6.

Fiber Preparation

1. Washing eight times boiling H_2O (with trace of NaOH wetting agent)
2. Distilled washing (four times) (room temperature)
3. Oven dry 120°C, eight hours
4. Fed into Ti/B CVD chamber

Fiber Feed-In Method	Results
1. Directly from air	No infiltration 6-24 in./min.
2. Closed yarn box feed-in	No infiltration 6-24 in./min.
3. Bake-out in air 200-500°C	Partial infiltration 6-10 in./min.
4. Bake-out in argon 200-500°C	Partial infiltration 6 in./min.

TABLE 4 SUMMARY OF WATER SOLUBILITY STUDIES TO REMOVE PVA SIZING

Burn-Off Furnace Atmosphere	Burn-Off Furnace Temperature °C	Fiber Throughput Maximum Speed in./min.	Infiltration Results
Argon	150	12	Partial infiltration
Argon	250	12	Better infiltration 50%
Argon	350	24	Full infiltration
Argon	450	18	Full infiltration
Argon	550	12	Partial infiltration
Argon	650	12	No infiltration
Argon	700	12	No infiltration
Nitrogen	250	12	Partial infiltration
Nitrogen	350	24	Full infiltration
Nitrogen	450	12	Full infiltration
Nitrogen	550	12	Partial infiltration
Nitrogen	650	12	No infiltration
Air	250	12	Full infiltration
Air	350	24	Full infiltration
Air	450	18	Full infiltration
Air	550	12	No infiltration

TABLE 5 SUMMARY OF PVA SIZING REMOVAL RESULTS USING PVA BURN-OFF FIBER TREATMENT

Precondition Furnace Atmosphere	Precondition Furnace Temperature Range °C	Fiber Throughput Maximum Speed in./min.	Infiltration Results
BCl_3/Ar	300 - 1000	18 - 24	Good infiltration. Little temperature effect on infiltration from 300 - 1000°C.
$TiCl_4/Ar$	300 - 700	12 - 18	No improvement
$BCl_3/TiCl_4/Zn$	600 - 700	18 - 24	No improvement
BCl_3/H_2	350 - 800	32 - 40	Excellent Infiltration. Little temperature effect on infiltration from 350 - 800°C.
$TiCl_4/H_2$	350 - 800	24 - 30	Good infiltration; not so efficient as BCl_3/H_2.
$BCl_3/TiCl_4/H_2$	350 - 1000	28 - 40	Good infiltration. No improvement over BCl_3/H_2 system.

TABLE 6 SUMMARY OF PVA SIZING REMOVAL RESULTS USING CHEMICAL TREATMENT

2.2.2.4 Combination Burn-Off/Chemical Treatment Process

The chemical treatment of the fiber tow was performed in a 2" OD clear quartz reaction tube, and evidence of a boron trichloride reaction with the water vapor from the decomposing PVA was observed. A white acidic precipitate formed at the exhaust when the T50 as-received fiber was fed directly into the reaction tube. By burning-off the fiber in air prior to entering the chemical treatment furnace, no such deposits were noticed. This led to the coupling of the burn-off furnace with the chemical treatment furnace as two distinct in-line operations necessary to condition the fiber surface prior to the deposition of Ti and B in the CVD reaction chamber. By drawing the as-received fiber through the in-line burn-off furnace, much faster operating speeds were attained, Table 7.

2.2.3 Ti/B Coating Zone Length

Concurrent with the engineering studies on sizing removal techniques, a series of experiments were performed to determine the effect of various zinc source lengths and increased gas concentrations on process operating speeds. In start-stop experiments, the yarn was placed in the reaction zone for various residence times and quickly pulled through the aluminum bath at 6 to 10 feet/minute. Points of infiltration were examined using a variety of gas flows and different length zinc sources. It was observed that, regardless of flow changes for the BCl_3 and $TiCl_4$, infiltration occurred over the zinc boat in all cases. For example, if a 12" zinc source were used at short residence times, the infiltrated length was 12", and so on. Using conventional surface treatment techniques during continuous operation, however, doubling the zinc zone did not necessarily double the operating speed at which wire could be produced during continuous operation. This suggested that the limiting factor in operating speed might be the fiber preparation prior to the Ti/B CVD reaction.

Different flow combinations and residence times were recorded, and results from the start-stop experiments are listed in Table 8. A schematic representation of the set-up used for the various conditions is depicted in Figure 6. Optimum results were obtained when both zinc boats were used and the $TiCl_4$ and BCl_3 were introduced at the furnace entrance. Under these conditions, good infiltration was observed with residence time as low as 30 seconds. Use of a longer zinc zone improved the wetting characteristics; however, distributing the $BCl_3/TiCl_4$ entrance within the chamber had little effect on the process.

2.2.4 Coupling of Fiber Pre-Treatment Process With an Increased Zinc Zone Length

The PVA burn-off and pre-treatment furnaces were coupled with the Ti/B coating chamber containing an increased zinc zone

Burn-Off Conditions		Chemical Treatment Conditions			Infiltration Results
Atmosphere	Temperature (^{o}C)	Atmosphere	Temperature (^{o}C)	Speed in./min.	
Air	250	$BCl_3/H_2/Ar$	350 - 800	40 - 44	1&2 Excellent infiltration, no effect noticed with increased temperature in chemical treatment furnace.
Air	350	$BCl_3/H_2/Ar$	350 - 800	42 - 50	
Air	450	$BCl_3/H_2/Ar$	350 - 800	12 - 18	3 Excellent infiltration, decrease in speed with increase in burn-off temperature.
Air	550	$BCl_3/H_2/Ar$	350 - 800	12	4 No infiltration at any speed.
Argon	350	$BCl_3/H_2/Ar$	350 - 800	40 - 48	5 Excellent infiltration, no speed increase with argon atmosphere in burn-off furnace.
Air	350	BCl_3/Ar	350 - 800	36 - 44	6 Decrease in speed without H_2 in chemical treatment furnace.
Air	350	$TiCl_4/H_2/Ar$	350 - 800	40 - 45	7 Excellent infiltration; $TiCl_4/H_2$ less effective than BCl_3/H_2 atmosphere in chemical treatment furnace.

TABLE 7 SUMMARY OF PVA SIZING REMOVAL RESULTS USING COMBINATION BURN-OFF/CHEMICAL TREATMENT

$TiCl_4/BCl_3$ Introduction at CVD Tube End	$TiCl_4/BCl_3$ Introduction at CVD Tube Center	Argon to Zinc Boat No. 1 (12" long zone)	Argon to Zinc Boat No. 2 (12" long zone)	Fiber Residence Time* (minutes)	Length of Infiltrated Fiber (inches)	Comments
on	on	on	on	5	19	Good infiltration(3)
on	on	on	on	4	18	Good infiltration(3)
on	on	on	on	3	18	Good infiltration(3)
on	on	on	on	2	18	Good infiltration(3)
on	on	on	on	1	0	Poor infiltration
on	off	on	on	4	24	Good infiltration(3)
on	off	on	on	3	18	Good infiltration(3)
on	off	on	on	2	18	Good infiltration(3)
on	off	on	off	4	11	Good infiltration(1)
off	on	on	off	4	12	Good infiltration(1)
on	off	off	on	4	12	Good infiltration(2)
high flow	off	on	on	5	24	Good infiltration(3)

*After stopping fiber, throughput speed for all trials 6-10 ft./min.

Apparent Results

1. $TiCl_4/BCl_3$ entrance point had little effect on infiltration
2. Direct correlation between zinc zone and infiltrated length
3. Increasing $TiCl_4/BCl_3$ flows decreased residence time needed for infiltration

(1) Fiber stopped over first zinc boat

(2) Fiber stopped over second zinc boat

(3) Fiber stopped over both zinc boats

TABLE 8 SUMMARY OF START/STOP INFILTRATION STUDY

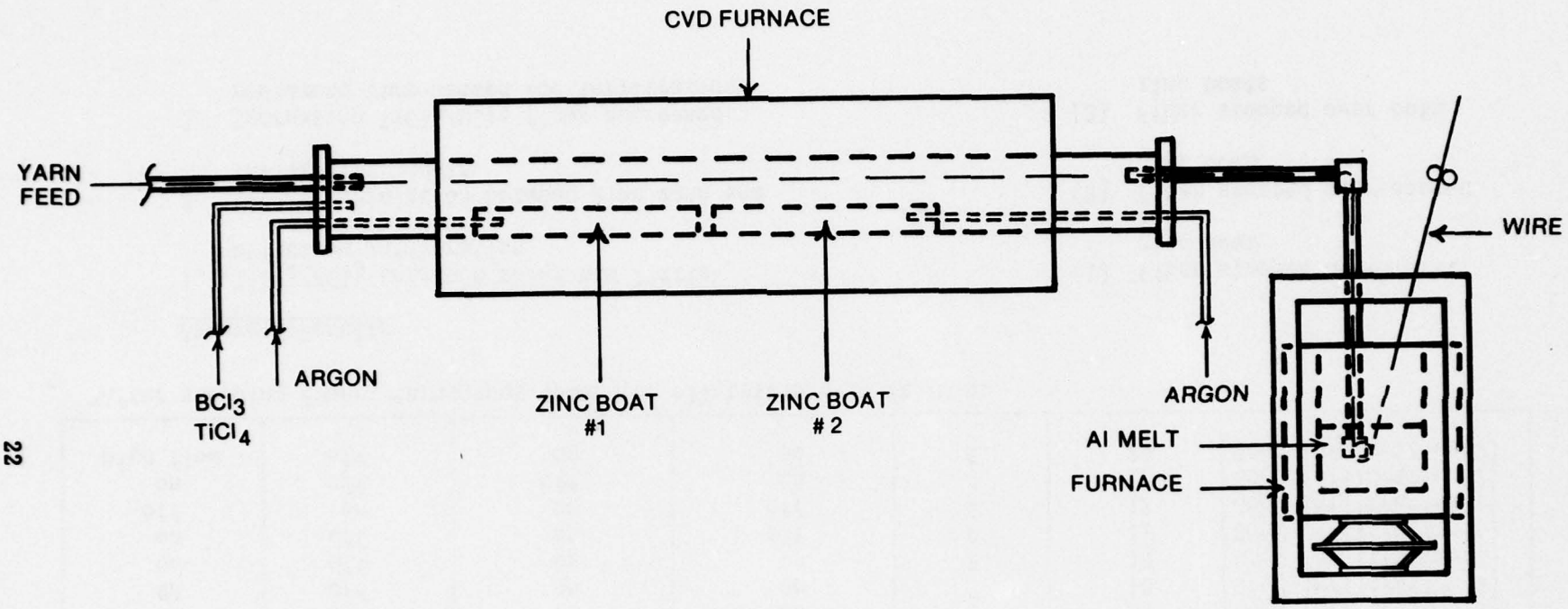


FIGURE 6

SET-UP FOR START/STOP ZINC ZONE STUDIES

length as depicted previously in Figure 3. The system brought together the most efficient fiber pre-treatment system with the most effective coating chamber. Optimization studies were performed on the process, and effects of process parameter changes on wire characteristics were determined. The system was assembled with versatility to introduce numerous flow changes into the system as well as to vary coating temperatures and speeds. For example, three reactant gas inlets were positioned to introduce the reactant gases in either the center hot zone or the ends of the Ti/B reaction chamber. The zone for the zinc vapor source was doubled with the versatility to operate with the entire zone or either half.

A summary of the various optimization studies performed is given in Table 9. Eight strand Thornel 50/A201 wire was produced at speeds approaching 60 inches/minute using this setup. The wire produced during this study was subjected to extensive testing and examination, the results of which are described in another section.

2.2.5 Effects of Nitrogen Instead of Argon Cover Gas

Nitrogen is available at a much lower cost than argon and, consequently, the possible use of N_2 instead of argon in the 1000 lb./year unit was investigated. Studies were performed to determine the effects of purging nitrogen instead of argon at critical places within the system. Nitrogen lines were set up to replace argon flows at the following positions:

(1) Yarn entrance to the Ti/B coating unit;
(2) Window box above the melt;
(3) End plate of the coating chamber.

After wire was being processed using an argon cover, nitrogen was substituted at one of these three critical areas, and the effects on aluminum infiltration were observed. Nitrogen, in all cases, immediately caused de-wetting of the fibers and, in effect, stopped the wetting process. Possibly, the nitrogen became involved in the reaction process within the Ti/B chamber altering the coating deposit on the graphite fibers. Design of the 1000 lb./year unit, therefore, proceeded using argon, and techniques for conserving argon usage were developed.

2.2.6 Fiber Handling

All previous graphite-aluminum wire from multistrand Thornel 50 fiber was made by rewinding the yarns from the cardboard supply reel onto a steel reel, burning off the PVA sizing in a batch process and placing the fiber into an argon purged "yarn box" for fiber feed into the Ti/B reaction chamber.

Air PVA Burn-Off	$BCl_3/H_2/Ar$ Preconditioning	Maximum Speed	Comments
250°C	200 - 650°	51 in./min.	As preconditioning furnace temperature increased above 400°C, infiltration speed decreased. Maximum speed was obtained at preconditioning temperature 350°C.
0 - 500°C	350°	60 in./min.	Maximum speeds obtained at 250-350°C PVA burn-off furnace temperature. Infiltration worsened at higher temperatures.

Optimum Parameters

Burn-off furnace 250-350°C
Precondition furnace 350°C

SUMMARY OF INFILTRATION RESULTS COUPLING BURN-OFF/CHEMICAL PRECONDITIONING FURNACES

TABLE 9 WITH INCREASED ZINC ZONE LENGTH

Inconsistencies in the composite wire due to "fuzz ball" formation or "loops" were observed upon operating the process over an extended period. These problems can be attributed to fiber build-up in the unit caused by friction within the transport mechanism due to non-uniform tension on individual fiber strands.

To verify this point, eight strands of Thornel 50 fiber were carefully wound onto a steel reel and drawn through a clear 2" ID quartz tube to simulate operating conditions of the existing laboratory graphite-aluminum unit. Separation of the fiber bundle was observed, and there were usually only one or two strands under uniform tension; the remaining fibers were carried through loosely. Strands would actually form small loops within the chamber and sag, causing the fiber to fray at the exit tube and eventually to break.

For the 1000 lb./year unit to successfully handle the fibers at increased speeds, it became apparent that uniform back tension would have to be kept on each individual strand of the fiber tow. The emergence of the fiber feed-in directly from the air allowed this improvement to be made. During design studies, eight separate plastic reels each containing a single strand of T50 fiber were used to supply fiber to the system. Constant tension on each reel eliminated the loose strand problem and aided in processing a more uniform composite wire with no handling problems. Also, an occasional strand break could be rectified by graphite cementing a splice without any appreciable process down time. A similar apparatus was incorporated in the 1000 lb./year unit design utilizing the cardboard reeled fiber as it was supplied by Union Carbide, eliminating any need for re-reeling fiber strands.

Larger diameter inlet and exit tubes, "O"-ring fittings on this tubing (to prevent indentations caused by swagelok ferrules), and transfer pulleys were also added in the fiber transport mechanism to lessen fiber friction and to improve handleability.

2.2.7 Testing Method

The preliminary graphite-aluminum composite wire produced during design studies using the apparatus described in Figure 3 at speeds ranging from 12 to 60 inches per minute was subjected to testing and examination. Tensile strength and modulus values were determined for the wire at each speed, and transverse wire sections were mounted for metallographic study of fiber distribution, wettability, and porosity. Chemical analyses of the matrix were made by the Chemical Testing Facility at FMI to determine if any impurities were present in the matrix following infiltration. The test method used to determine strength and elastic modulus was accomplished in accordance with specification NAVSEA 0900-080-0010 and is included in the appendix section. Problems were encountered in using nylon cord tabs to grip the specimen. The woven nylon cord twisted the test specimen as tension was applied, causing the

graphite-aluminum to fail prematurely due to shear forces. This was particularly noticeable on early samples when the specimens were of a flatter configuration. A series of tests were performed using both nylon cord and fiberglass tubes to further examine the test method. In most cases, the nylon-held composites failed prematurely except when the sample configuration was uniformly round.

Metallographic work was performed on the wire to evaluate fiber distribution, wettability, and porosity within the composite. Micrographic preparation of the wire involved mounting, grinding, rough polishing, and final polishing for examination and photography. Each mount was impregnated in a clear epoxy resin mixture under atmospheric conditions and held in place by an aluminum ring. The hardened surface was then ground by hand on a rotating wheel using a water lubricant and progressing from 320 to 600 grid metallographic polishing paper. Nylon or metcloth positioned on a rotating wheel with one micron diamond paste lubricant was used to rough polish the samples by hand, and final polishing was accomplished using microcloth and a 0.05 micron alumina lubricant. Micrographs of transverse and longitudinal sections for further analysis were taken on positive Polaroid black and white film. Specimens are presently on file in the Testing Laboratory at FMI.

Chemical analysis of the aluminum matrix was performed on an Echelle Grating Argon Plasma Emission Spectrometer - Spectraspan 111. Blanks of an HC1, HNO_3, H_2O mixture were used to dissolve standard samples from a certified A201 ingot and also test samples from the A201 melt and graphite reinforced wire. Using the standard and blank, a working curve or linear range was determined and used at a given wave length for each element in question.

2.2.8 Test Results

The preliminary tensile and modulus properties (Table 10) indicate that increased speeds did not decrease the wire properties, suggesting that adequate Ti/B coatings were deposited on the fiber to prevent degradation by aluminum. More extensive testing was obtained on wire produced during optimization studies of the actual 1000 lb/year unit, and wire strengths and moduli increased as defects such as voids were eliminated as the process was optimized.

Variations in tensile results were observed using the two grip technique mentioned earlier. These differences were noticed throughout the program on identical production runs of graphite reinforced wire tested at FMI's Mechanical Testing Facility. In tests using the nylon rope gripping technique described in NAVSEA Handbook 0900-080-0010, the specimen ends twisted approximately 180° prior to tensile failure. This twisting certainly contributed substantial shear forces over the one inch gage length and probably caused premature failure. A comparison of typical tensile values using both flexible nylon grips and fixed fiberglass tabs is made in Table 11.

Experiment No.	C-13, T-2	C-15, T-14	C-15, T-15	C-16, T-48	N-30, T-16	N-30, T-3
Composite Wire Properties						
Operating speed (in/min)	12	24	30	60	40	51
Melt residence time (sec)	20	10	8	4	15	12
Cross-sectional area ($in^2 \times 10^{-5}$)	187	183	170	180	157	156
Diameter ($in \times 10^{-3}$)	48	48	46	48	45	45
Volume percent fibers	27	28	30	28	33	33
Breaking load (lbs)	172	163	208	190	183.4	183.4
Modulus (msi)	24	25	24	21	22	22
Tensile strength (psi)	92,000	89,000	123,000	106,000	117,000	117,000

Approximate no. of fibers: 11,500
Average wire density: .0840 lb/in^3

TABLE 10 THORNEL 50/A201 COMPOSITE PROPERTY SUMMARY FOR VARIOUS THROUGHPUT SPEEDS

All Wire From Study No. N-13-16

Fiber:	Thornel 50
Matrix:	A201 Alloy
Volume percent fiber:	30
Rule-of-mixture tensile strength:	90,000 psi*

Mil. Spec. No. 0900-080-0010

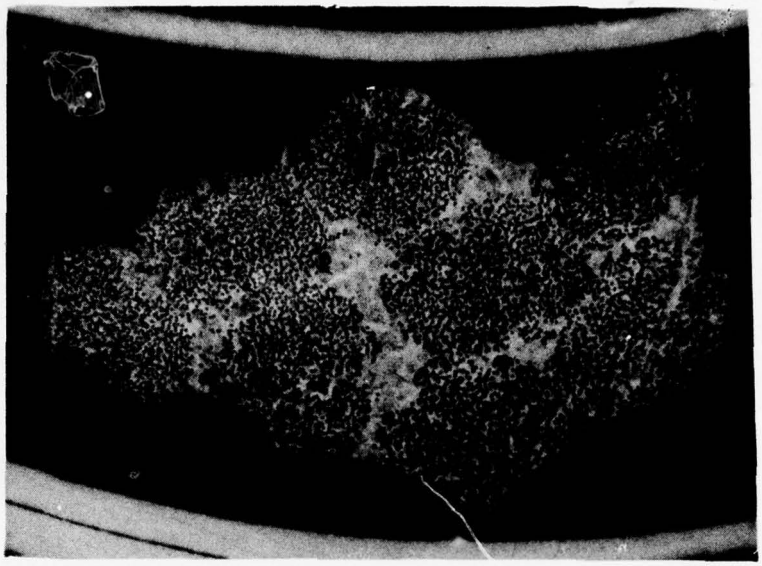
(Nylon Rope Tabs; 1" Gage Length)	(Fixed Fiberglass Grips; 4" Gage Length)
92,200 psi	119,000 psi
95,200 psi	118,000 psi
90,400 psi	114,000 psi
92,000 psi	111,000 psi
Pull-out	108,000 psi

*Using fiber bundle strength of 244,000 psi

TABLE 11 COMPARISON OF TENSILE RESULTS FROM TWO SPECIMEN GRIPPING TECHNIQUES

Noticeable in the micrographs of the wire produced during the studies were void formations between the fiber strands, which became more prevalent at higher infiltration speeds (Figures 7-10). At speeds of 60 inches/minute, the coated fiber had a residence time of approximately four seconds in the aluminum melt, which probably was not adequate time to allow outgassing of chlorides carried over on the coated fibers (from the Ti/B CVD reaction chamber). Wire was made under identical operating conditions except that the residence time in the melt was increased to approximately 10 seconds by infiltrating the coated fiber in a deeper melt. Micrographs of wire produced at 40 and 51 inches per minute (Figures 11 and 12) using a longer residence time had a pronounced effect on the integrity of the wire, specifically void and porosity formation.

Chemical analyses were done to assure that the aluminum matrix composition fell within the A201 alloy specification as described in Table 12. Matrix analyses have also been included in Table 12. In all cases, the graphite-aluminum matrix fell within the required specification of the alloy.



Transverse Section

EXPERIMENT NO. C-13, T-2 MAG. 63.5X

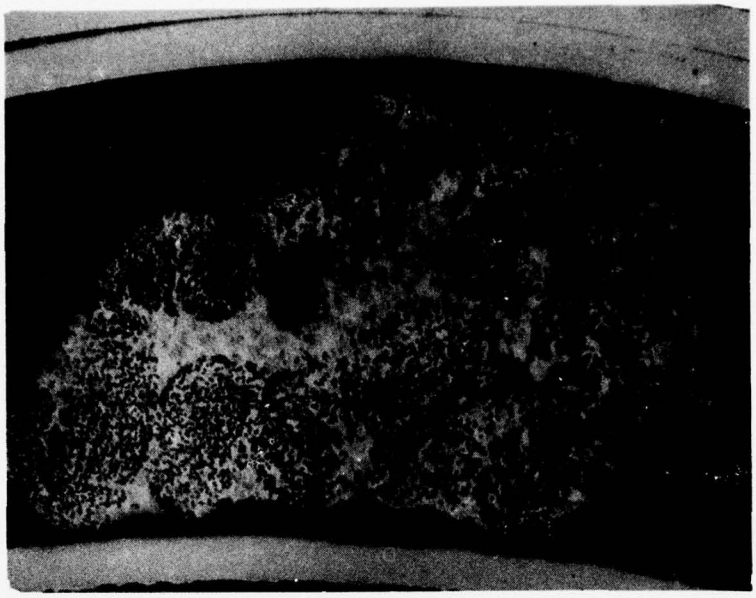
Composition:

Graphite Fiber:	Thornel 50
Total Number of Fibers:	11,500
Aluminum Alloy:	A201
Volume Percent Fibers:	27

Operating Parameters Using Experimental Scale-Up Unit (Figure 3)

Wire Production Speed:	12 in./min.
Fiber Residence Time in Melt:	20 seconds

FIGURE 7 GRAPHITE-ALUMINUM COMPOSITE WIRE



Transverse Section

EXPERIMENT NO. C-15, T-14 MAG. 63.5X

Composition:

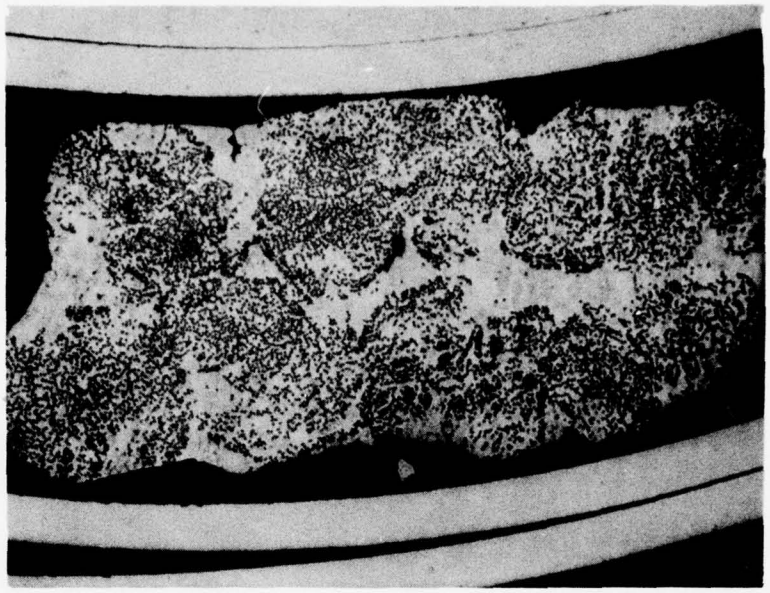
Graphite Fiber:	Thornel 50
Total Number of Fibers:	11,500
Aluminum Alloy:	A201
Volume Percent Fibers:	28

Operating Parameters Using Experimental Scale-Up Unit (Figure 3)

Wire Production Speed:	24 in./min.

Fiber Residence Time in Melt: 10 seconds

FIGURE 8 GRAPHITE-ALUMINUM COMPOSITE WIRE



Transverse Section

EXPERIMENT NO. C-15, T-15 MAG. 63.5X

Composition:

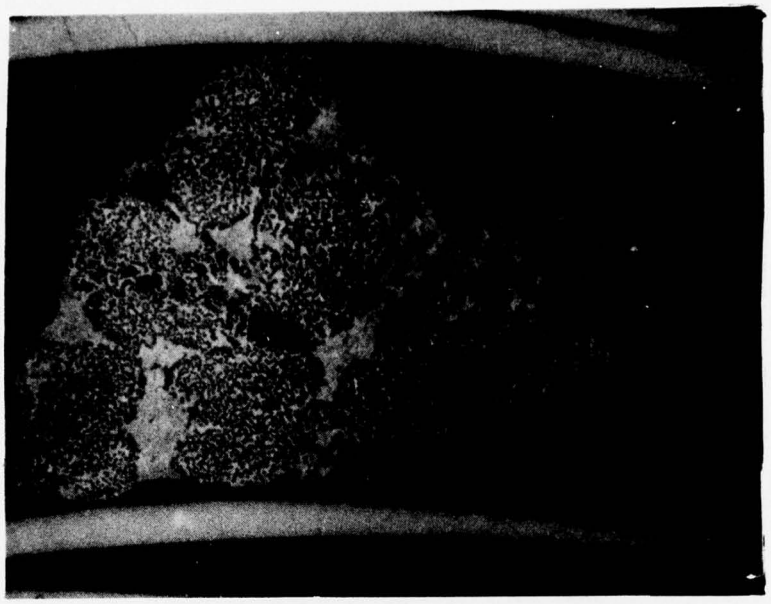
Graphite Fiber:	Thornel 50
Total Number of Fibers:	11,500
Aluminum Alloy:	A201
Volume Percent Fibers:	30

Operating Parameters Using Experimental Scale-Up Unit (Figure 3)

Wire Production Speed: 30 in./min.

Fiber Residence Time in Melt: 8 seconds

FIGURE 9 GRAPHITE-ALUMINUM COMPOSITE WIRE



Transverse Section

EXPERIMENT NO. C-16, T-48 MAG. 50X

Composition:

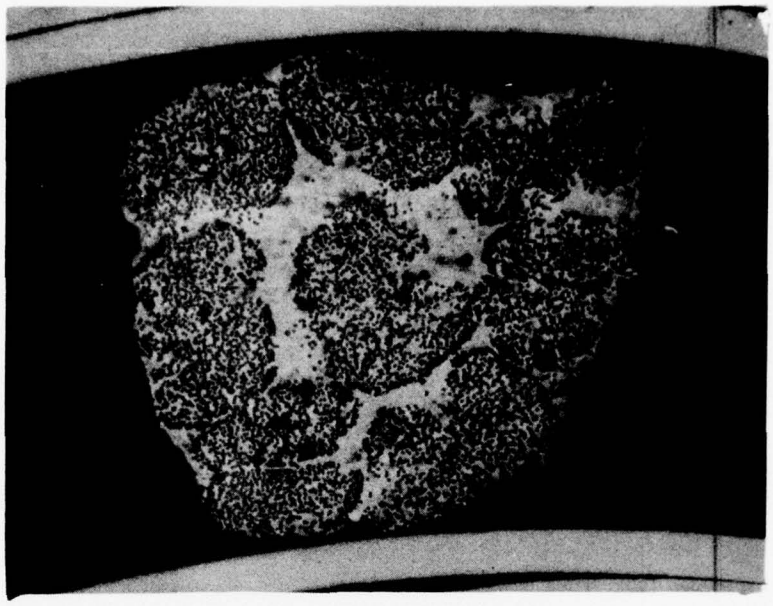
Graphite Fiber:	Thornel 50
Total Number of Fibers:	11,500
Aluminum Alloy:	A201
Volume Percent Fibers:	28

Operating Parameters Using Experimental Scale-Up Unit (Figure 3)

Wire Production Speed: 60 in./min.

Fiber Residence Time in Melt: 4 seconds

FIGURE 10 GRAPHITE-ALUMINUM COMPOSITE WIRE



Transverse Section

EXPERIMENT NO. N-30, T-16 MAG. 63.5X

Composition:

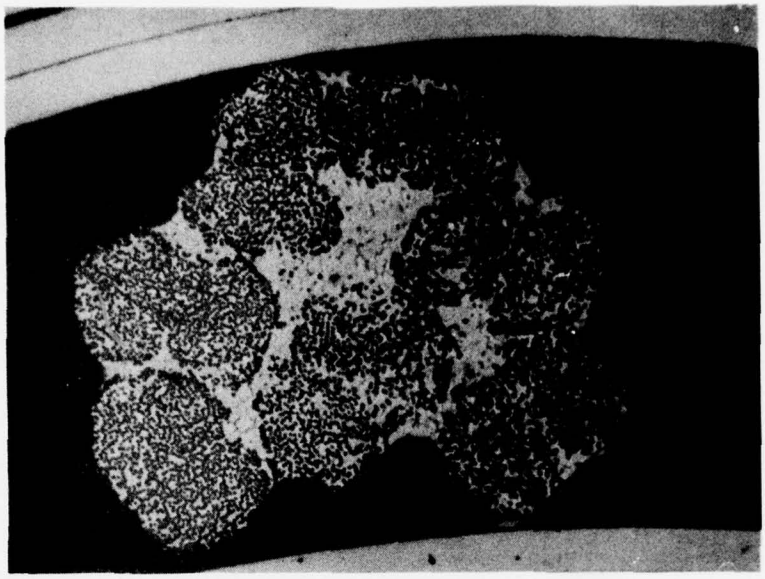
Graphite Fiber:	Thornel 50
Total Number of Fibers:	11,500
Aluminum Alloy:	A201
Volume Percent Fiber:	33

Operating Parameters Using Experimental Scale-Up Unit (Figure 3)

Wire Production Speed: 40 in./min.

Fiber Residence Time in Melt: 15 seconds

FIGURE 11 GRAPHITE-ALUMINUM COMPOSITE WIRE



Transverse Section

EXPERIMENT NO. N-30, T-3 MAG. 63.5X

Composition:

Graphite Fiber:	Thornel 50
Total Number of Fibers:	11,500
Aluminum Alloy:	A201
Volume Percent Fiber:	33

Operating Parameters Using Experimental Scale-Up Unit (Figure 3)

Wire Production Speed:	51 in./min.

Fiber Residence Time in Melt: 12 seconds

FIGURE 12 GRAPHITE-ALUMINUM COMPOSITE WIRE

	A201 Ingot	Matrix of T50/A201 Wire
Al (aluminum)	Bal	Bal
Ag (silver)	0.5	0.47
B (boron)	---	None detected
Cu (copper)	4.7	5.5
Fe (iron)	0.02	0.023
Mg (magnesium)	0.3	0.32
Ti (titanium)	0.17	0.2
Zn (zinc)	---	Present
Hg (mercury)	---	None detected
Si (silicon)	0.03	Not determined
Mn (manganese)	0.27	0.36

TABLE 12 ELEMENTAL ANALYSIS OF A201 INGOT AND MATRIX

SECTION 3

CONSTRUCTION OF THE 1000 LB./YEAR UNIT (TASK I)

3.1 GENERAL SCOPE

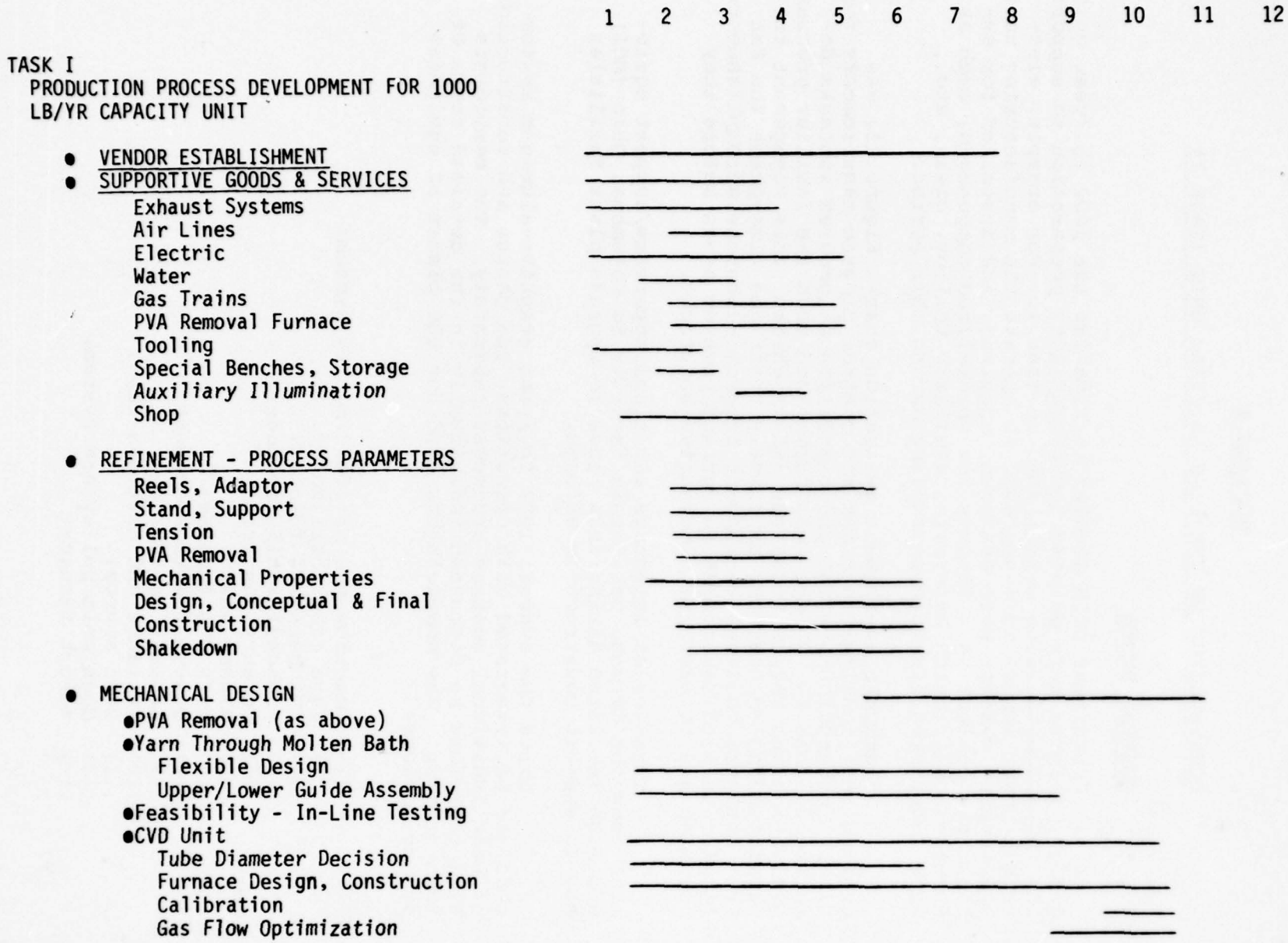
Concurrent with studies to finalize the 1000 lb./year unit design, efforts were devoted toward facility preparation to support the requirements being established in Task I. For example, electrical power imputs were upgraded to operate the manufacturing unit, and venting systems were designed, acquired, and installed for exhaust gas collection. Vendors for specialized components, such as furnace construction materials, auxiliary tooling, gases, etc., were identified for future ordering during this period.

A graphic management evaluation chart, Figure 13, was drafted and finalized to track and control program requirements for timely integration/phasing and completion of program subtasks detailed in Task I. Though less formalized than the familiar program evaluation and review technique (PERT) charts, this management tool permitted the contractors to closely track and time-phase the Man Tech subtasks required to support program milestone accomplishments. It also enabled management to surface problem areas before they occurred and to exercise alternative solutions.

Transfer of selective technical apparatus/support equipment from the Carson, California facility to Columbus, Ohio (MCI) was also initiated during this phase to upgrade plant facilities and to support construction efforts.

Since the overall 1000 lb./year graphite-aluminum system consists of integrated unit operations, the design and construction of each individual section proceeded separately. The components will therefore be discussed individually in the detailed scope of this section. The nomenclature used for the pieces of equipment are as follows:

(1) Reaction gas manifold/mixing system;
(2) Yarn creel/collimator;
(3) PVA burn-off furnace;
(4) Preconditioning furnace;
(5) Mercury gas trap;
(6) Window box;
(7) Ti/B CVD furnace;
(8) Quartz reaction chamber;
(9) Exhaust system;
(10) Entrance and exit end caps;
(11) Zinc source;
(12) Open melt pulley arm system;
(13) Retort furnace.


1 2 3 4 5 6 7 8 9 10 11 12
TASK I
PRODUCTION PROCESS DEVELOPMENT FOR 1000 LB/YR CAPACITY UNIT
• VENDOR ESTABLISHMENT
• SUPPORTIVE GOODS & SERVICES
Exhaust Systems
Air Lines
Electric
Water
Gas Trains
PVA Removal Furnace
Tooling
Special Benches, Storage
Auxiliary Illumination
Shop
• REFINEMENT - PROCESS PARAMETERS
Reels, Adaptor
Stand, Support
Tension
PVA Removal
Mechanical Properties
Design, Conceptual & Final
Construction
Shakedown
• MECHANICAL DESIGN
•PVA Removal (as above)
•Yarn Through Molten Bath
Flexible Design
Upper/Lower Guide Assembly
•Feasibility - In-Line Testing
•CVD Unit
Tube Diameter Decision
Furnace Design, Construction
Calibration
Gas Flow Optimization

- Crucible Furnace
  - Design Decision
  - Construction
  - Determine Fluxing Needs

- CHEMICAL DESIGN
  - Preliminary Pilot Parameters
  - Activated Zone
  - Tube Geometry, Flows
  - Throughput
  - Iterative Design
  - Design Meeting

TASK II
PROCESS OPTIMIZATION STUDY LEADING TO DEVELOPMENT OF A **2000** LB/YR UNIT

DESIGN HIGH CAPACITY UNIT
- Evaluate 1000 lb/yr Unit
- Parameter Modification
- Consideration of Automation
- Design Meeting
- Graphics & Description

TASK III
PRODUCTION & DELIVERY OF 100 LBS GR-AL WIRE

- Specification Verification

TASK IV
REPORTING & DOCUMENTATION

- Monthly Reports
- Quarterly Reports
- Final Report

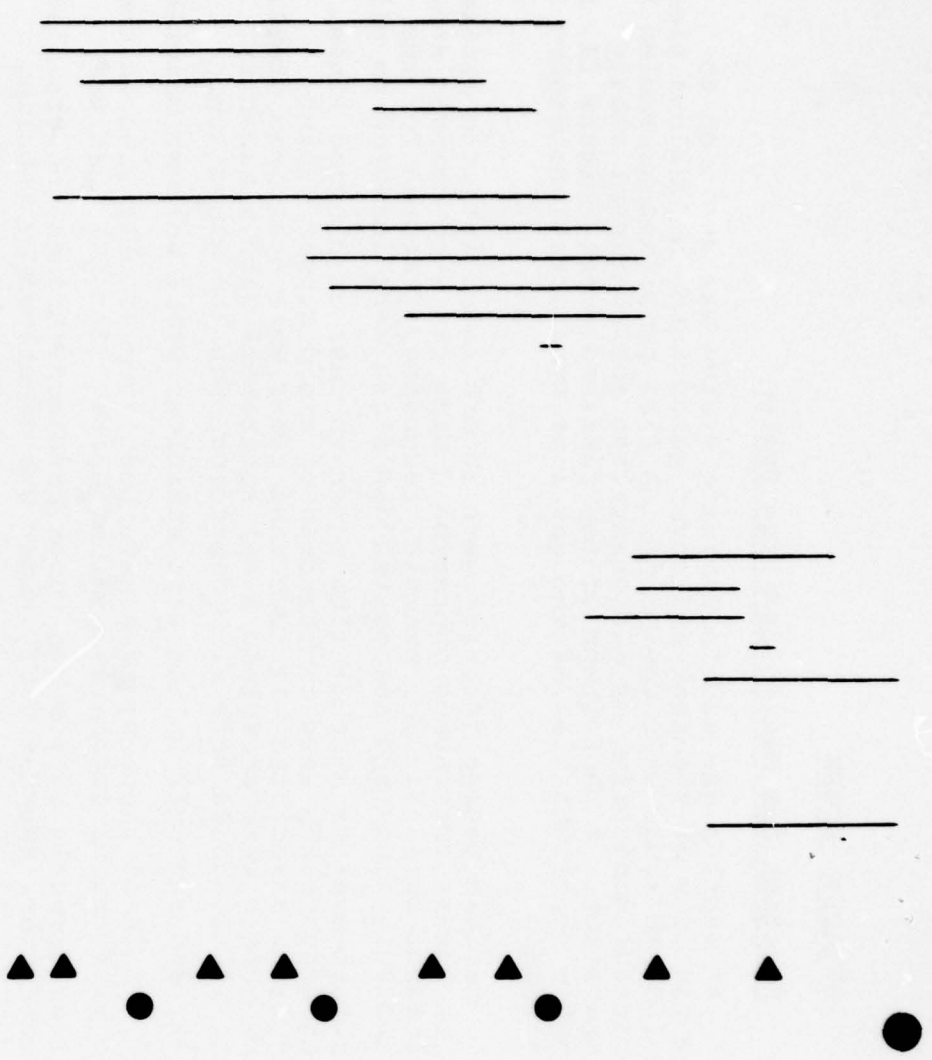


FIGURE 13 MANUFACTURE OF GRAPHITE-ALUMINUM COMPOSITE PRECURSOR WIRE

3.2 DETAILED SCOPE

3.2.1 Reaction Gas Manifold/Mixing System

A reaction gas manifold/mixing system was designed to control the flow of reactant and cover gases into the various pieces of the 1000 lb./year unit equipment. A flow panel was assembled to allow careful monitoring of gas quantities for continual steady state operation. A photograph of the finished panel, Figure 14, and a schematic representation of the gas line configuration, Figure 15, are included.

Certain design features were incorporated into the manifold system to assure continuous operation during gas feed changes and/or line cleanout periods. For example, redundancy features for the $TiCl_4$ and BCl_3 lines and associated gas flows were inserted to allow quick switch-over to another flow meter in case of clogged lines. Incoming argon lines were constructed of rigid copper tubing, whereas lines associated with reactant gases were stainless steel. All flow meters were stainless steel rotameters with a capacity range of .0084 to 104 scfh air (depending upon the glass tube insert[1]), and shut-off valves were stainless steel bellows metering valves[2]. Both of these systems have been successfully used in the past on pilot plant graphite-aluminum units. The BCl_3 gas was controlled directly by its own vapor pressure through the stainless steel rotameter, whereas $TiCl_4$ vapor was generated by bubbling argon through liquid $TiCl_4$ and monitoring the exiting argon saturated with the $TiCl_4$ vapor.

The gas manifold/mixing system, when assembled, underwent extensive shakedown including vacuum checking and purging with pure argon prior to operational trials. This procedure was mandatory since a slight leak in the manifold or gas delivery system could introduce oxygen into the system which would be detrimental toward the wetting of the fiber by aluminum.

3.2.2 Yarn Creel/Collimator

A yarn creel/collimator was designed to allow easy access to the fiber spools while providing uniform back tension to all strands in the fiber tow, Figure 16. Basically, this apparatus permits the as-received yarn spools to be directly loaded onto spindles and to be collimated into multistrand tows. Back tension is controlled by adjustable spring tension devices located at the base of the apparatus. Initial transfer operational studies indicated the necessity for uniform back-tensioning of the individual

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1. Matheson Series 7600 - 150mm

2. Nupro Bellow Metering System

FIGURE 14 REACTION GAS MANIFOLD/MIXING PANEL

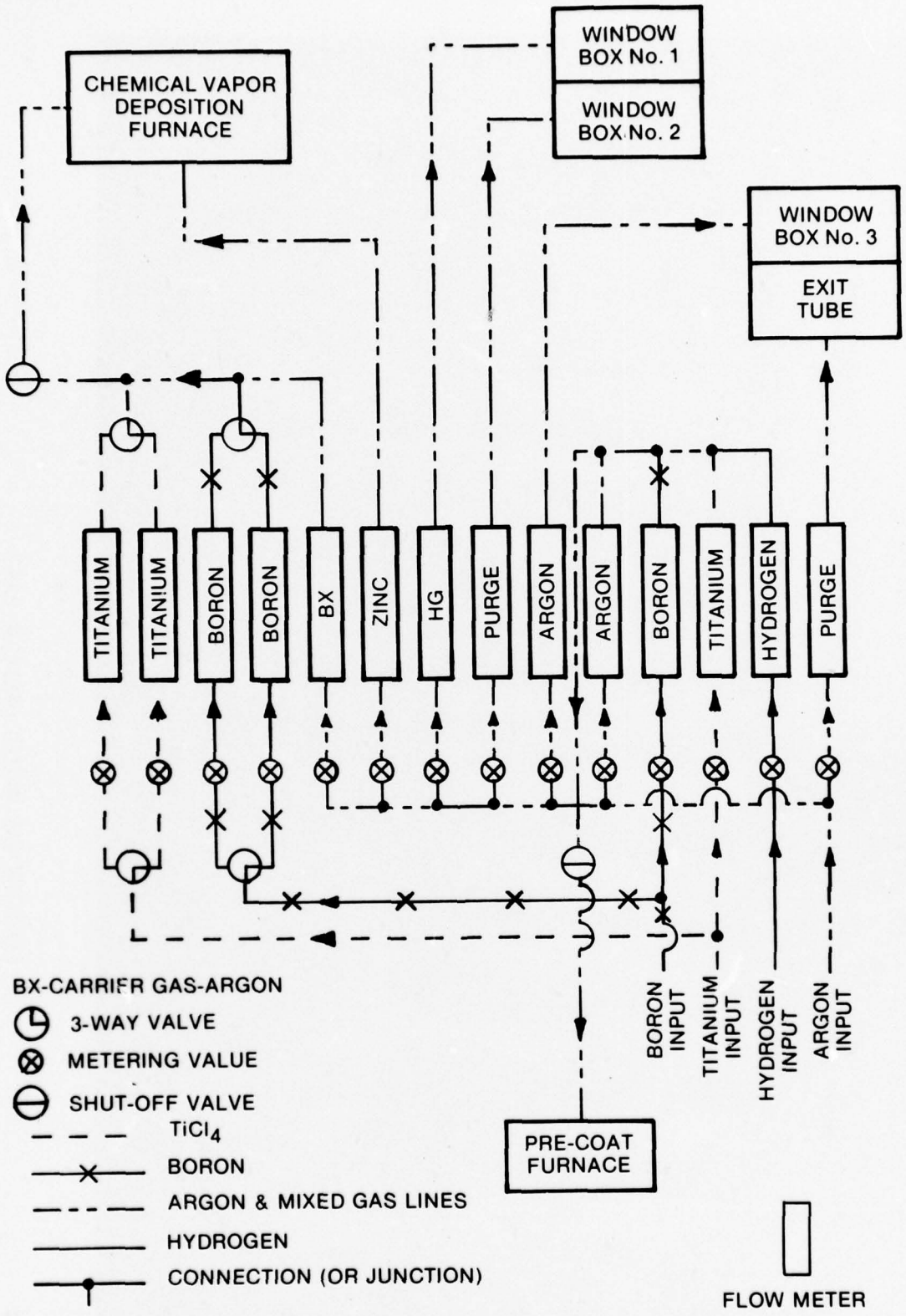


FIGURE 15 **GAS LINE CONFIGURATION**

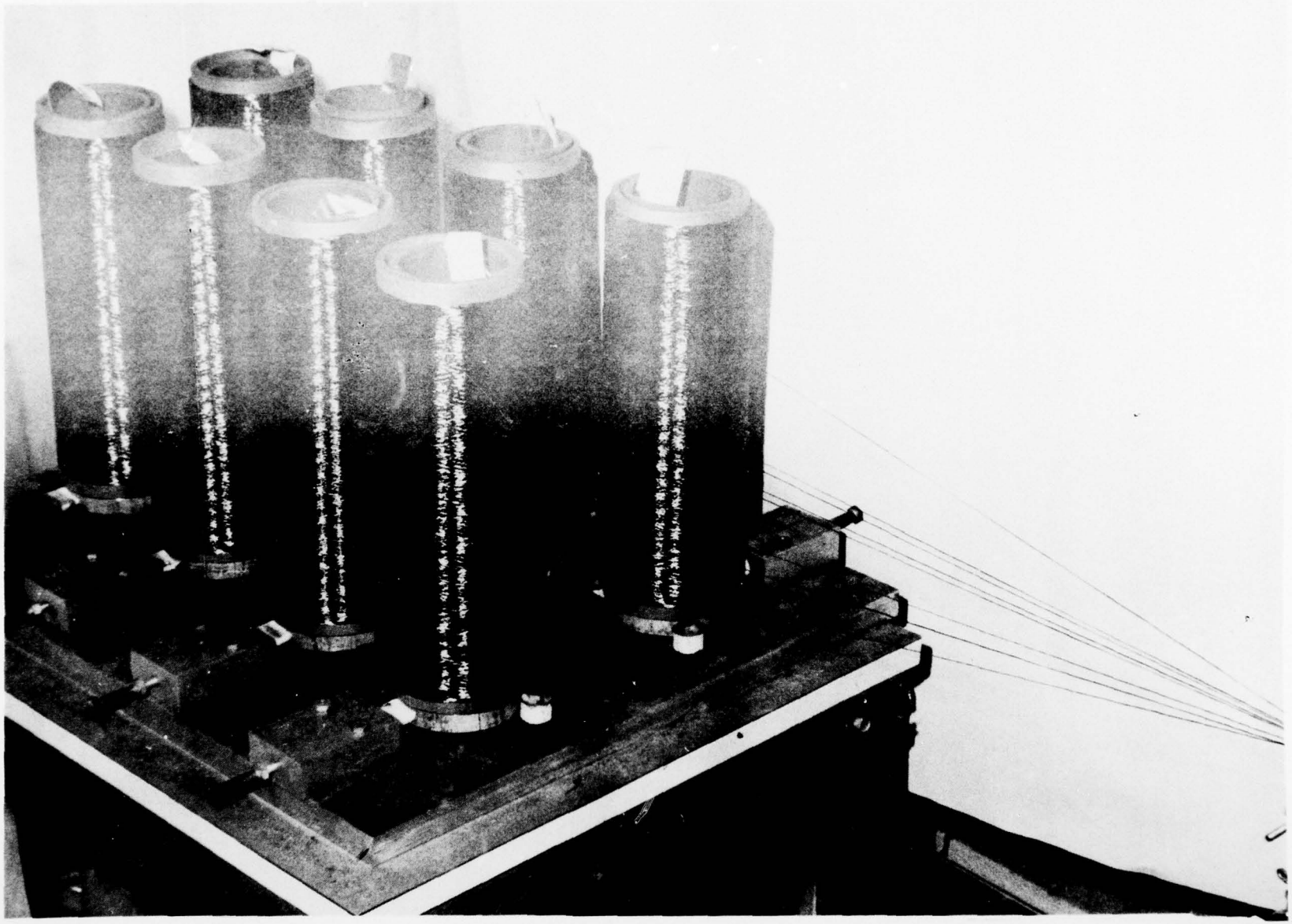


FIGURE 16 YARN CREEL/COLLIMATOR

strands to prevent fiber draping and, therefore, rubbing in the various chambers. This procedure offered several advantages over previous yarn handling techniques wherein the as-received single strand yarns were rewound on a single spool as an eight strand tow. This former technique did not permit uniform tensioning of the individual yarns, which in turn caused the formation of loops and the separation of strands within the processed wire.

The collimator was designed to allow easy removal and replacement of reels during operation (from the top).

3.2.3 PVA Sizing Burn-Off Furnace

The PVA burn-off furnace is needed to remove the PVA sizing and other surface impurities prior to chemical preconditioning of the yarn bundle. Design efforts focused on simplicity, low cost, and ease of operation.

The unit consists of a four foot long hot zone with temperature capability of 500°C, Figure 17. A one inch Pyrex tube is wrapped with heat tape, insulated with Kaowool blanket, and held in place by a stainless steel cover. Three thermocouples are positioned at the glass surface to monitor temperature using a cyclic controlling device.

To prevent fiber rubbing inside the glass tube, the eight separate strands were consolidated through reducing eyelets prior to entering the furnace. Care was taken to keep any fiber strand at an angle less than 15° from the horizontal plane to assure even back tension at all times.

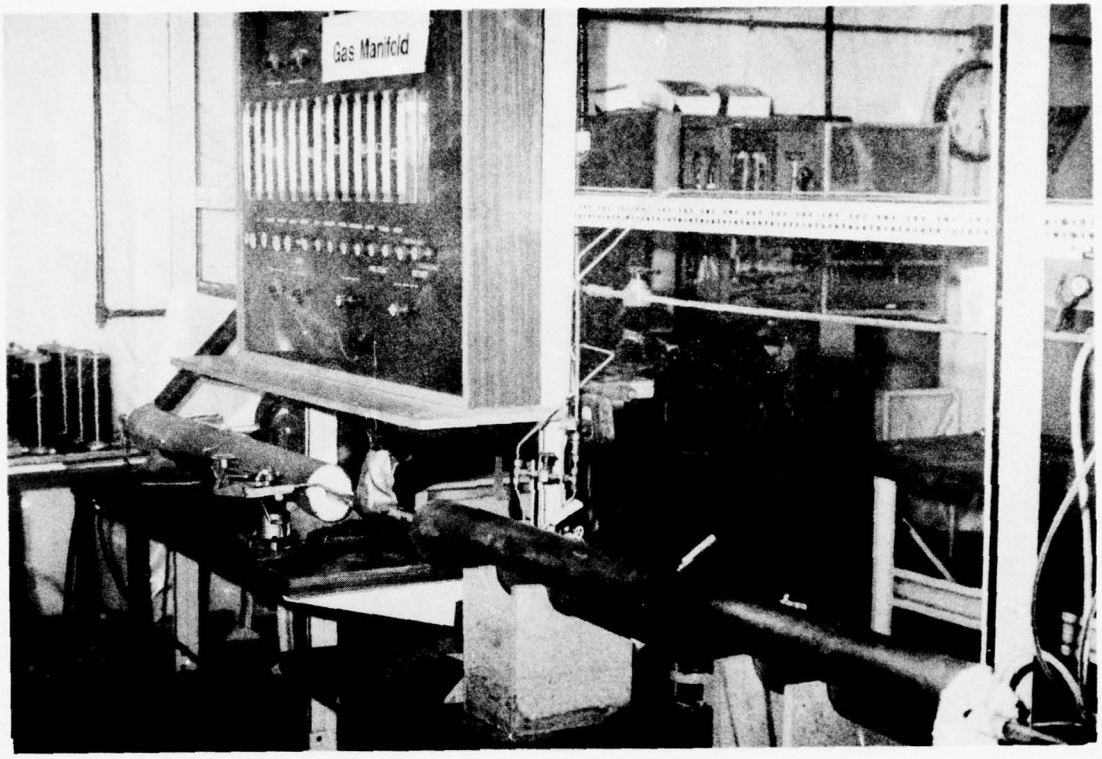
3.2.4 Fiber Preconditioning Furnace

The fiber preconditioning furnace treats the fiber surface prior to entering the CVD coating chamber by further removing remaining traces of PVA or impurities from the fiber surface, thus increasing production speeds of wire formation.

The preconditioning furnace is similar in construction to the PVA furnace, Figure 17, with a slightly longer hot zone (5.5 feet) and provisions for maintaining a throughput of reactant gases. The fiber is fed into the hot zone through a one inch diameter glass tube also acting as a counter-current gas exit port. The reaction tube is connected directly to a mercury trap separating it from the Ti/B chamber and has the capacity to accept BCl_3, $TiCl_4$, H_2 and Ar gases.

3.2.5 Mercury Gas Trap

A mercury gas trap was designed to isolate the atmosphere of the fiber treatment furnace from the gases in the reaction furnaces. The mercury trap also effectively decreases the quantity



PVA Burn-off Furnace

Preconditioning Furnace

FIGURE 17 FIBER TREATMENT FURNACES

of argon needed in the process. Design studies indicated that mercury did not interfere with the chemical process nor did it contaminate the graphite-aluminum composite product. Proper venting equipment was installed to exhaust any traces of mercury or mercury chlorides.

3.2.6 Window Boxes

Window boxes are closed containers needed to maintain an inert atmosphere for the coated fibers between the various process units. The boxes were designed to transport fiber in the following areas:

(1) Between preconditioning furnace and Hg trap;
(2) Between Hg trap and Ti/B furnace;
(3) Between Ti/B furnace and aluminum melt.

Inside the box is a pulley system which is needed to change the fiber throughput direction 90^{o} without causing fraying or degradation.

3.2.7 Ti/B CVD Reaction Furnace

The Ti/B reaction furnace was constructed to heat the quartz reaction chamber for CVD coating prior to liquid metal infiltration. Design study determined that a five foot heating zone would adequately coat the fiber bundle at the required operating speed.

The furnace consists of a three zone system with a thermac controlled 40 inch center zone and thermoelectric controlled 12 inch end zones, Figure 18. Clam shell elements are used to facilitate opening the furnace for removal of the quartz tube during cleaning. A winch was installed above the furnace top to lift the top section of the furnace during cooling down and reaction tube replacement periods.

3.2.8 Quartz Reaction Tube

A quartz reaction tube was chosen over its inconel counterpart because of its availability, lower cost, and compatibility with the reacting gases. The tube has a 5" OD and extends eight feet in length. The only machining requirement was a polished OD approximately 1½" from each end to allow a good seal between the reaction chamber and each end cap. A quartz exhaust tube (1/2" OD) was fused approximately 12" from one end at right angles to the reaction chamber for removal of spent reaction gases during operation. Figure 18 shows the quartz tube positioned inside the CVD furnace with the brass end caps in place.

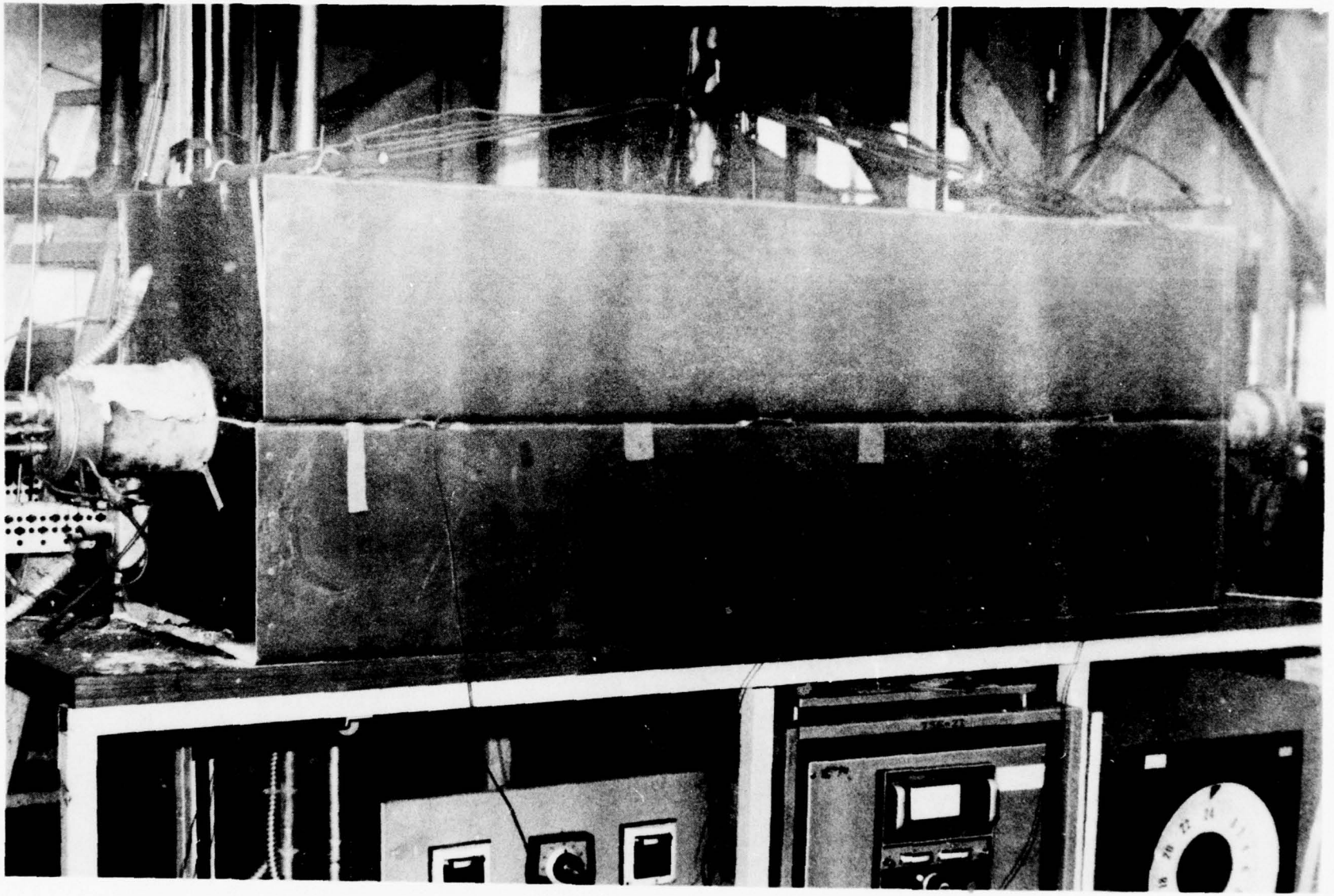


FIGURE 18 TI/B CVD REACTION FURNACE

3.2.9 Exhaust System

Spent reaction gases are exhausted through a 1/2" OD tube fused onto the reaction chamber and are collected through a venting system. Other such reactants are exhausted at the yarn extrances to both the PVA removal furnace and preconditioning furnace. Proper venting was also installed in the vicinity of the aluminum melt during melt purification runs. To prevent the exhaust gases from clogging up at the 1/2" exit tube, an oscillating spring mechanism was inserted into the tube, thus maintaining the open port. Further improvements in the exhaust system were suggested during optimization studies for the 2000 lb./year unit.

3.2.10 Entrance and Exit End Caps

End caps for the quartz reaction chamber were designed to allow adequate seals and easy removal for fast clean-up. The caps were machined from brass and provide an O-ring seal between the sides of the caps and quartz tube.

3.2.11 Zinc Source

Zinc vapor is supplied for the Ti/B reaction from a graphite boat positioned in the hot zone of the quartz chamber. The vapor is forced through holes located in the lid of the container and is helped through with an argon carrying gas. In pilot plant units, the boat consists of a graphite fixture to hold molten zinc, which has to be removed from the reaction chamber when the supply becomes depleted, causing production shut-down. The boat is also costly due to machining requirements and the high quality of graphite needed.

For these reasons, a simpler tube configuration was adopted which could be constructed from either graphite or quartz at a much lower cost (Figure 19). The tube was also designed to extend four feet into the hot zone for a more even zinc distribution. Also, by connecting the zinc tube to the end plate via a 1/2" OD stainless steel tube, zinc sticks could be continually added through the 1/2" opening to replenish the zinc source. Problems, however, developed in balancing the zinc vapor with the other reactants in the system. These problems were dealt with during the optimization study and are discussed in that section.

3.2.12 Open Melt Pulley Arm System

The open melt pulley arm system has previously been schematically represented in Figure 5. This apparatus allows the use of an aluminum melt open to the atmosphere rather than closed under an argon purge, thus facilitating such operation as yarn rethreading, aluminum melt cleaning, and melt level control.

The unit consists of a 3/4" OD titanium tube which extends from the window box into the aluminum melt. On the aluminum

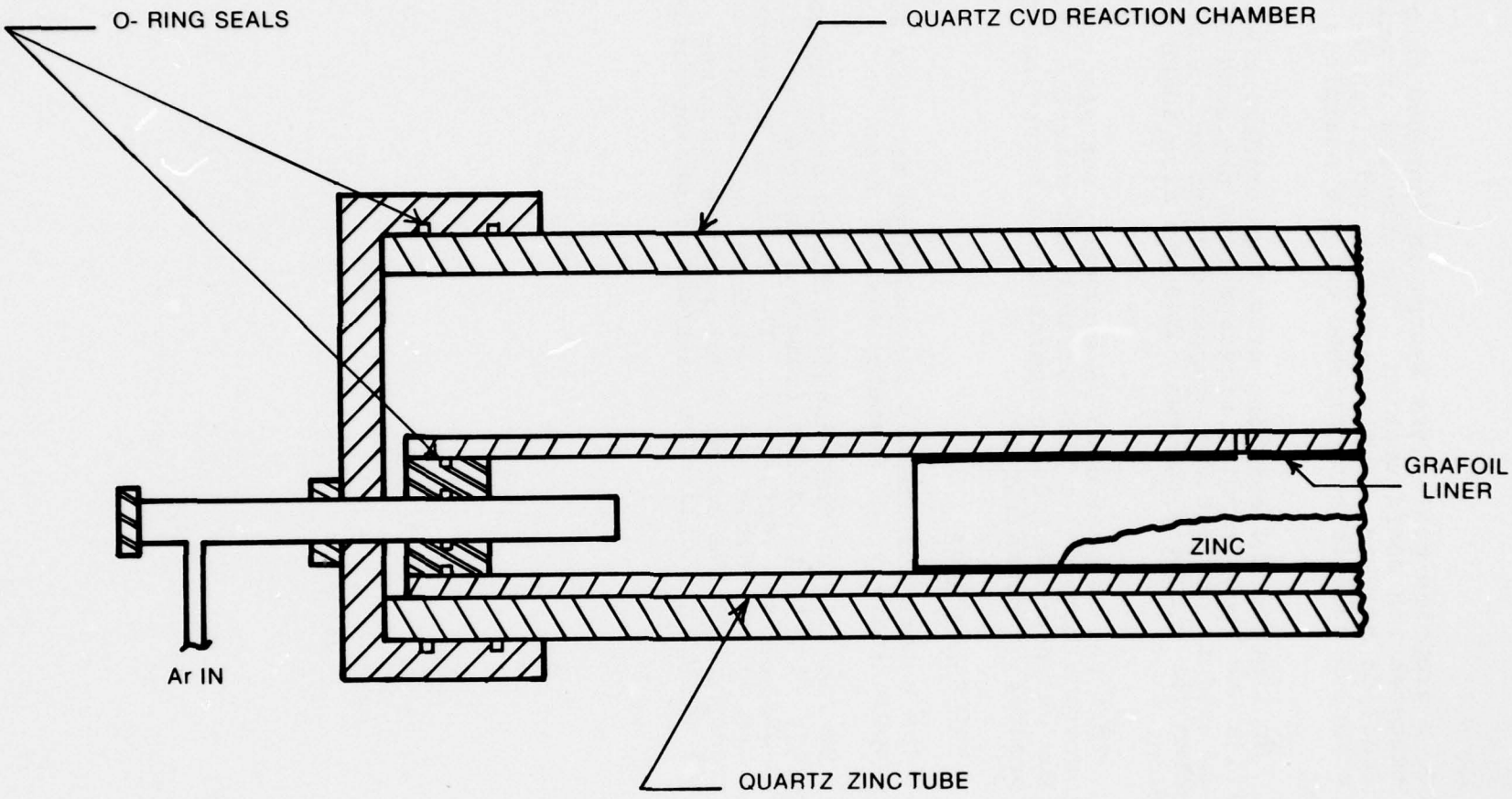


FIGURE 19 **ZINC TUBE CONFIGURATION**

melt end, a graphite pulley arm system is fastened onto the tube with a tungsten rod configuration. The tube end is oxidized to retard reaction between the aluminum melt and titanium. Cooling of the titanium tube is accomplished using a stainless steel air jacket.

To prevent the existing wire from oxidizing as it leaves the melt, a one inch diameter titanium tube prepared in a similar manner is used to collect the composite under an inert atmosphere. A mechanism for aligning the two tubes was also added during production.

This set-up proved to be extremely satisfactory for the present system; however, a more durable arm material is being sought for extended periods of operation in future units with larger production capabilities.

3.2.13 Retort Furnace

The retort furnace was assembled to accept a SiC melt crucible approximately 10" diameter and 15" deep.

To facilitate fiber handling during start-up and break-down periods, a retort furnace frame was designed to be movable both horizontally and vertically. The vertical movement is needed to raise the melt crucible and, therefore, to submerge the pulley system transporting the coated fiber into the aluminum. The horizontal movement facilitates melt/arm alignment during operation.

SECTION 4

OPTIMIZATION STUDIES LEADING TOWARD 2000 LB./YEAR PAN GRAPHITE-ALUMINUM UNIT (TASK II)

4.1 GENERAL SCOPE

Optimization studies were performed on the 1000 lb./year unit to evaluate the efficiency of the process and to determine changes that would be required to expand its capacity. Operating parameters were varied, and effects of these variations were investigated. Equipment design was critically tested, and changes were made during this period whenever modifications benefited wire production. A critical analysis of the unit was made, and problem areas were cited. Design meetings were held to discuss various problem areas, and suggestions for improvement were recorded for further capacity improvement. Many of these suggestions have been applied to the conceptual design of the 2000 lb./year unit.

Optimization studies on the 1000 lb./year unit leading to the design of a larger capacity unit concentrated on the following areas:

(1) Equipment evaluation;
(2) Parameter study;
(3) Automatic control of conditions.

4.2 DETAILED SCOPE

4.2.1 Equipment Evaluation

4.2.1.1 Manifold/Gas Mixing System

The gas mixing manifold system performed well in support of the 1000 lb./year unit, and most of the design concepts will be duplicated for future manufacturing plants.

One problem that was experienced with the manifold system was an occasional backup of $TiCl_4$ liquid into the argon supply lines. This situation occurred when the pressure of the argon supply fell below the pressure being maintained within the $TiCl_4$ storage tank. Corrective action was taken by installing check valves in gas lines, thus desensitizing the $TiCl_4$ system to argon pressure changes. Additionally, a valve arrangement for the $TiCl_4$ reservoir was positioned in the line which enabled it to be purged and cleaned with pure argon. An independent system for filling

the $TiCl_4$ reservoir should be incorporated in future units, thus eliminating any chance of backup due to check valve failure.

The concentration of $TiCl_4$ being carried into the system depends upon its saturation level in argon. Increases in $TiCl_4$ vapor levels were attained by adding stainless steel screens into the liquid container to maximize surface area and also to break up the bubbling argon into finer components. Efficiency improvements were noticed immediately.

A problem inherent in supplying $TiCl_4$ vapor in the manner mentioned is that the vapor pressure and, therefore, concentration of $TiCl_4$ introduced, depends largely upon the atmospheric temperature. For example, between 21.8°C and 34.2°C, the vapor pressure of $TiCl_4$ increases from 10mm to 20mm Hg. Variations in temperature easily reach this magnitude in a typical production facility; therefore, concentrations of $TiCl_4$ entering the system will also fluxuate. Suggested methods to more accurately control incoming $TiCl_4$ in the 2000 lb./year unit included: 1) isothermal packing surrounding $TiCl_4$ tank and lines into the system, 2) supplying $TiCl_4$ into the system utilizing its own vapor pressure, 3) adding $TiCl_4$ liquid into the chamber by a controlled "drop" method. Further design studies for the 2000 lb./year unit will determine which above method will best support the process.

4.2.1.2 Yarn Creel/Collimator

The yarn creel/collimator performed satisfactorily, maintaining equal back tension on each fiber reel (Figure 16). No changes in a fiber feed mechanism are anticipated for the 2000 lb./year unit.

4.2.1.3 PVA Sizing Burn-Off Furnace

Time proportional controllers were originally used to maintain the temperature of the PVA burn-off furnace. The nature of controller required on/off periods during operation which caused an uneven temperature environment for yarns being processed. The time proportional controllers were therefore replaced with a powerstat (steady state) power supply which improved temperature control significantly. Readings in both cases were monitored through an indicating pyrometer.

The overall performance of the PVA burn-off furnace was good. The 2000 lb./year unit will require a larger fiber transport tube to prevent any chance of fiber tows rubbing during operation; however, an increase in zone length is not anticipated.

4.2.1.4 Fiber Preconditioning Furnace

The fiber preconditioning furnace used to prepare the T50 fibers prior to the Ti/B coating step in the process will not be adequate for the 2000 lb./year PAN graphite-aluminum unit. The more active PAN based fibers undergo thermal degradation and attack by aluminum unless they are protectively coated before being drawn through the CVD reaction chamber. The present preconditioning unit does not afford this protection to PAN based fibers.

Work at FMI has led to the development of high temperature CVD protective coatings for PAN graphite, resulting in excellent translation of fiber properties in aluminum. This coating technique will be substituted for the preconditioning furnace and placed in the same position of the overall process. Further optimization steps will be required to increase the volume capacity of this operation before it can be placed in line for the 2000 lb./year unit.

4.2.1.5 Mercury Gas Trap

The mercury trap successfully maintained the seal between the Ti/B furnace and the preconditioning unit without degrading the graphite fibers during operation. In transporting the fiber bundle, a graphite pulley was utilized to draw the fibers through the mercury trap.

Although no problems were noticed using the mercury trap, it was suggested that another type of seal be used for the 2000 lb./year unit to 1) eliminate the two 90^{o} fiber bends required with the present set-up, 2) eliminate possible danger source from any traces of mercury being transported into the hot reaction chamber.

4.2.1.6 Window Box Construction

The window boxes adequately guided the fiber through the three 90^{o} turns required in the transport mechanism. Boron nitride leads were inserted during optimization studies to prevent the possibility of any strands jumping the pulleys and also to allow a smooth transport with minimum friction.

For the 2000 lb./year unit, it was suggested that all pulley systems except that above the aluminum melt be eliminated. This would be beneficial during high speed operation in that the fiber would undergo only one 90^{o} bend prior to infiltration.

4.2.1.7 Ti/B CVD Reaction Furnace

The CVD furnace was rebuilt during the program due to a materials incompatibility which caused a center zone burn-out. The problem was rectified, and a new center zone was installed.

Performance of the five foot zone furnace was evaluated, and the following conclusions were reached concerning the design:

(1) The five foot zone will adequately coat fiber at a 1000 lb./year capacity;

(2) Design changes should be made to accomplish faster heat-up to operating temperature, thus decreasing down time;

(3) Process parameter variations within a five foot zone will allow a 2000 lb./year unit to be designed without increasing the coating zone length.

4.2.1.8 Quartz Reaction Tube

The quartz CVD reaction tube performed well during the program, and a similar chamber will be utilized in the 2000 lb./year design. Excellent seals were obtained between the end caps and OD of the quartz tube. Also, subsequent cleanup operations demonstrated that the quartz reaction tube cleaned as well as, if not better than, its inconel counterpart presently used in other pilot plant units.

4.2.1.9 Entrance and Exit End Caps

The entrance/exit end caps performed extremely well during optimization and production runs, and no major design changes are anticipated for the 2000 lb./year unit.

4.2.1.10 Zinc Source

Zinc vapor is used to reduce the metal chlorides in the Ti/B CVD reaction and is supplied from a zinc source located within the quartz chamber. In past units, the zinc container consisted of an enclosed graphite boat over which the yarn bundle was transported. Three 3/16" holes were drilled in the boat lid to allow the zinc vapor to escape, and argon gas was also used to help carry the zinc vapor through these exit holes. One problem inherent in this system was the fact that the boat could not be replenished with zinc when the supply was depleted. This meant that the reaction chamber would require clean-out whenever the zinc supply ran out.

A zinc tube was therefore designed for the 1000 lb./year unit which 1) extended the zinc zone from 18" to 48" and 2) allowed a method for replenishing the tube with metal (Figure 19).

A tube configuration was also chosen so that the graphite could be replaced with quartz, since quartz is non-reactive with

molten zinc. It was thought that elimination of graphite pieces from the chamber would reduce impurities caused by graphite outgassing within the reaction zone and, thus, increase operating speeds.

During shakedown tasks, however, several operational subtleties were revealed concerning the increased size of the zinc boat. The initial configuration, a four foot long, 1½" diameter graphite tube with 16 1/8" exit holes for zinc vapor, proved to be over-efficient; that is, the concentration of zinc vapor was so high that it did not permit balancing with the $TiCl_4$ and BCl_3 reactant gases. At operating temperatures in excess of 660°C, the pressure of zinc rose rapidly and exceeded the capability of the manifold to balance the reaction with other gases. Thus, a zinc rich condition did not permit satisfactory infiltration. Through a series of iterative empirical trials involving both better temperature controls (hence, better zinc vapor pressure control) as well as restricting the number of vapor holes in the zinc tube, the reaction was balanced and wire was produced. Further investigation in the 1000 lb./year unit revealed that wire speeds using traditional zinc boats were as fast as, if not faster than, those with the zinc tube; therefore, the zinc boat used on pilot plant units was inserted for the production cycle. It was also discovered that zinc boats could be "hot changed" during operation, thus allowing the zinc to be replenished without requiring a complete unit cleanup.

One difference between the two zinc systems, which could account for the speed variations, was the concentration of zinc vapor leaving each of the exit holes. In the long tube configuration, the argon helper entered from one end and traveled through the tube to the opposite end of the 48" tube located in the hot zone. Flow studies revealed that argon leaving each hole appeared to be relatively constant; however, due to the length of the tube, the concentration of zinc leaving the furthest hole was much greater than that from the hole nearest to the argon source. This meant that the fiber would see an excess of zinc vapor prior to entering the melt which could have had an adverse effect on wetting characteristics.

Three methods for introducing zinc vapor into the system have been suggested as possible alternatives to the present system for future unit design:

(1) External zinc vapor generating source;

(2) Introduction of zinc powder directly onto the fibers;

(3) Modification of present zinc boat to allow means of continually replenishing zinc supply and to maintain constant zinc surface area during operation.

Further optimization studies on the zinc vapor supply mechanism should be performed on future manufacturing plant designs to assure careful control of zinc quantities and also to allow continuous operation without need to shut down production to replenish the zinc supply.

4.2.1.11 Open Melt Pulley Arm System

As mentioned in Section 3, the final melt arm design consists of an oxidized titanium tube with a graphite pulley assembly attached and completely submerged in the aluminum melt (Figure 5). This arm successfully maintains the inert atmosphere around the coated fiber and withstands the temperature and the attack by molten aluminum quite well. No problems are anticipated in transferring this method into the 2000 lb./year unit. During extended runs, the oxidized titanium tube is eventually attacked by the aluminum and becomes an expendable item. Studies will therefore proceed to find better materials with a longer life span for the 2000 lb./year unit operation.

4.2.1.12 Retort Furnace

The retort furnace and frame mechanism performed well during the program, and no changes in the unit are anticipated for scale-up to a 2000 lb./year unit.

4.2.2 Parameter Study

The 1000 lb./year unit underwent extensive parameter study during operation to optimize wire quality and speed. Both temperature and flow control in the Ti/B reaction chamber had pronounced effects on attainable speeds and will be a critical factor in developing larger capacity units. Melt purification techniques were investigated, and suggestions for the 2000 lb./year unit were made.

4.2.2.1 Ti/B CVD Reaction Chamber

Refinement studies in the Man Tech CVD furnace indicated that the quantity of zinc vapor necessary to reduce the chlorides was directly dependent upon the flow of argon carrier gas over the molten zinc, the surface area of exposed molten zinc and, naturally, the temperature of the CVD unit. The control of zinc vapor within the unit was critical towards the balance of the gas flows and reaction. Therefore, balancing the unit for production cycles and increased operating capacity required control of these interdependent factors. For example, considerable lack of reproducibility occurred if argon flow was carefully monitored without careful control of the temperature of the zinc boat. Higher operating temperatures caused increases in zinc vapor pressure which, in turn, increased the concentration of zinc in a constant argon carrier gas flow. Consequently, both internal thermocouples

(within the CVD chamber, in proximity to the zinc boat) as well as external thermocouples were utilized to bracket acceptable balances between these critical factors of zinc boat temperature and argon flow through the zinc boat.

Also, zinc quantities were found to depend upon the surface area of molten metal exposed to the argon purge. Using zinc holding tubes, for example, as the zinc supply was depleted, the surface area also decreased due to the geometry of the tube. This factor influenced the reaction gas balance and required changes in argon carrier gas flows and temperature to compensate.

Future zinc boat design for the 2000 lb./year unit, as discussed previously, will be needed to optimize reaction kinetics within the CVD unit. Further design studies will be required to determine the most controllable zinc system for the reaction zone. Critical design features include:

(1) Accurate temperature control,
(2) Maintenance of constant surface area;
(3) Constant vapor concentration;
(4) Continuous zinc replenishing system.

4.2.2.2 Melt Purification

Considerable effort was made to purify the aluminum melt during operation and to determine the expected "life" of a given production melt. It is generally recognized that liquid metals can absorb considerable amounts of gases. Two well-known characteristics of aluminum melts are 1) the tendency to absorb hydrogen and 2) the reaction with oxygen to form oxides and dross. Hydrogen is readily soluble in molten aluminum; however, during solidification, a marked decrease in solubility occurs. Thus, during rapid solidification of graphite-aluminum wire, it is possible to trap hydrogen and to form pores in the matrix. Also, since an open melt technique is employed, it is necessary to address the possible formation of oxides.

In addition to melt purification techniques, attempts were made to eliminate possible hydrogen sources from the system. The following potential hydrogen containing areas were investigated:

(1) Graphite fiber;
(2) Graphite fixtures;
(3) Argon contamination;
(4) Oxygen/hydrogen atmosphere above melt.

The primary hydrogen source from the graphite fibers was the PVA sizing on the individual filaments. During the PVA burn-off cycle, most of the sizing was thermally decomposed and consequently removed. Since the decomposition involved the formation of water molecules, however, there was a possibility that traces of water were still present in the yarns. The addition of the BCl_3 preconditioning furnace aided in removing most of these impurities.

Due to the outgassing nature of graphite parts upon heating, attempts were made to eliminate graphite fixtures from all coating units. In particular, the zinc boat in the CVD reaction tube was replaced with a quartz tube to lower the impurity level in the chamber. However, problems in balancing the reaction gases using a zinc tube configuration were encountered as mentioned in previous sections. This forced the temporary removal of the quartz zinc tube and the return of the graphite boat into the 1000 lb./year unit. Attempts will be made to remove this last remaining graphite fixture from the 2000 lb. unit.

Liquid gas cylinders were used to supply argon to the infiltration system. To prevent contaminants in the argon, such as hydrogen or oxygen traces, from entering the unit, a titanium chip getter was installed in the 1000 lb./year argon supply line. Results were very satisfactory.

Melt cleaning techniques such as solid anhydrous active metal chlorides and non-oxidizing gas fluxes were considered to remove gas impurities from the unit melt. Solid flux techniques were not deemed feasible because of their tendency to become entrapped in the molten aluminum and to introduce new gases due to impurities in the fluxes themselves. Also, the possibility existed for these metal fluxes to find their way into the titanium tube containing the coated fibers which could have had an adverse effect on the wetting process.

Gas fluxes such as metal halides, chlorine, nitrogen, argon, and helium have been process effective in the aluminum industry and are easier to administer. Various combinations of these gas fluxes were bubbled into the aluminum melt to remove hydrogen and other impurities. The most effective method for purifying the aluminum was a combination of chlorine/argon gas. The bubbling gases carried hydrogen and other impurities out of the melt, and surface inclusions were skimmed off the melt surface.

Considerable thought was also given toward the expected "life" of a production melt. Although melt levels were maintained by constant replacement with fresh ingot aluminum, the question arose as to whether or not a melt maintained the limits of the specified starting material during extended runs. Part of the Ti/B coating on the transported fiber, along with zinc vapors, dissolved in the aluminum during production of wire. To assure

that these additions did not cause the A201 melt to fall outside specification limits, the melts were fully charged periodically. Melt and wire compositions were examined after given periods to determine the necessity of total replacement.

4.2.3 Automation Study

Automation studies revealed at least four critical areas in the graphite-aluminum wire operation that required either a worker to be present and oversee the procedure or the production unit to be shut down. The 1000 lb./year unit was designed to minimize these inefficiencies and also to allow future improvements to be made in these areas on units with larger capacities. The operations needing maximum monitoring included:

(1) Fiber transport system;
(2) Melt control and purification techniques;
(3) Exhaust clean-out;
(4) Reaction gas control mechanisms.

4.2.3.1 Fiber Transport System

An important feature of the 1000 lb./year unit was the improvement in the fiber transport system. The closed yarn box, for example, was replaced with a yarn creel apparatus which held individual strands of the T50 fiber under equal back tension. This improvement not only increased wire consistency, but also allowed fiber changing without excessive down time. Yarn splicing, although not yet automated, was also much easier to implement due to the open end fiber feed set-up. By simply graphite bonding a new fiber yarn to the existing tow, the operator could change the fiber in a matter of minutes.

This new system, coupled with larger transport tubes, boron nitride leads, and an open melt configuration, has helped to minimize fiber handling problems. Future improvements to be considered for the 2000 lb./year unit include:

(1) Automatic fiber splicing;
(2) Automatic fiber threading system into the unit;
(3) Fully automated wire collection device.

4.2.3.2 Melt Control and Purification Techniques

Present aluminum level control, melt replenishing, and purification are done manually on the 1000 lb./year unit. An hydraulic melt lift system, which has facilitated the melt leveling procedure considerably, was designed and inserted into the unit. At accelerated speeds, melt leveling and replenishing became a

critical operation toward maintaining consistent wire. Large additions of solid aluminum alloy to the existing melt, for example, lowered the overall melt temperatures and affected the wire surface characteristics.

Melt purification techniques, such as gas bubbling, were successful but required a brief operational shutdown to perform. For the 2000 lb./year unit, a method for continually adding aluminum to the melt and purifying the same should be designed. An automatic leveling/purifying system would assure homogeneity of the melt and consistency of wire. This type of addition would also free the operator to concentrate on other unit areas.

4.2.3.3 Exhausting

The exhaust system was essentially automatic, since spent gases were collected through a 1/2" exit port which was kept open by use of either a spring or auger device. The problem with the exhaust actually existed within the reaction chamber where the spent gases condensed onto the CVD reaction tube. As these exhaust products accumulated on the walls of the chamber, they eventually "choked off" the opening used to transport the fiber. At this point, a unit clean-out was required.

Extensive thought was given toward development of an automatic tube exhaust cleaner which could break up this accumulation and prevent clog-up. Such a system would eliminate the need to clean up the CVD chamber and would decrease down time by at least a factor of three. Attempts will be made to develop such a cleaning device for the 2000 lb./year unit.

4.2.3.4 Reaction Gas Control

The reaction gas control, as described for the 1000 lb./year unit, was very adequate and required little monitoring of flow meters. Problems in maintaining constant zinc and titanium tetrachloride concentrations were not caused by variations in flow control, but by variations in vapor pressures. Methods to stabilize temperatures at which zinc and titanium tetrachloride vapors are generated should be developed to assure accurate monitoring of reactant gas quantities. Such systems will be designed for the 2000 lb./year unit.

SECTION 5

CONCEPTUAL DESIGN OF THE 2000 LB./YEAR PAN GRAPHITE-ALUMINUM UNIT (TASK II)

5.1 GENERAL SCOPE

Services were performed on the existing process leading to the conceptual design of a single unit that would produce 2000 lbs. of PAN graphite-aluminum wire per year. Focus was placed on increasing production capacity, improving fiber transport, and lowering the cost of operation; i.e., decreasing "down time" while increasing reaction efficiency. Modifications were also required to accept PAN based graphite fibers into the system instead of the rayon based fibers used this year.

Generally, commercially available PAN based graphite fibers are more handleable than their rayon based counterpart and, therefore, more amenable toward transport through the liquid metal infiltration process. For example, Union Carbide Corporation's Thornel 300 fibers in a 6000 filament tow have been successfully infiltrated using existing equipment without the fraying or fiber breakage problems often encountered using Thornel 50. Similar results have been obtained using other PAN fibers ranging from 1000 to 10,000 filament tows with 35 to 50 million modulus and 300 to 400 Ksi tensile strength.

Many of the PAN fiber tows are factory coated with a resin compatible sizing rather than polyvinyl alcohol, which does not have an adverse effect on wetting. These fibers can therefore be infiltrated at speeds similar to T50 without the need of a pre-conditioning unit prior to entering the Ti/B furnace.

In the past, PAN fibers underwent both thermal and chemical degradation during the Ti/B coating process and subsequent liquid metal infiltration. Recent barrier coatings have been developed that protect the fibers from degradation and also improve their already excellent handleability. The barrier coatings act in a manner similar to organic sizings by consolidating fiber tows. This is especially useful when infiltrating the line of "non-sized" PAN based fibers.

The sectional view of the 2000 lb./year design concept is depicted in Figure 20. Four separate 6 to 10,000 filament tows will be simultaneously coated in the Ti/B chamber and wetted by aluminum. The following modifications have been suggested for the 2000 lb./year unit:

(1) Four separate fiber tows;
(2) Square or rectangular zinc sources;
(3) Rectangular shaped reaction chamber.

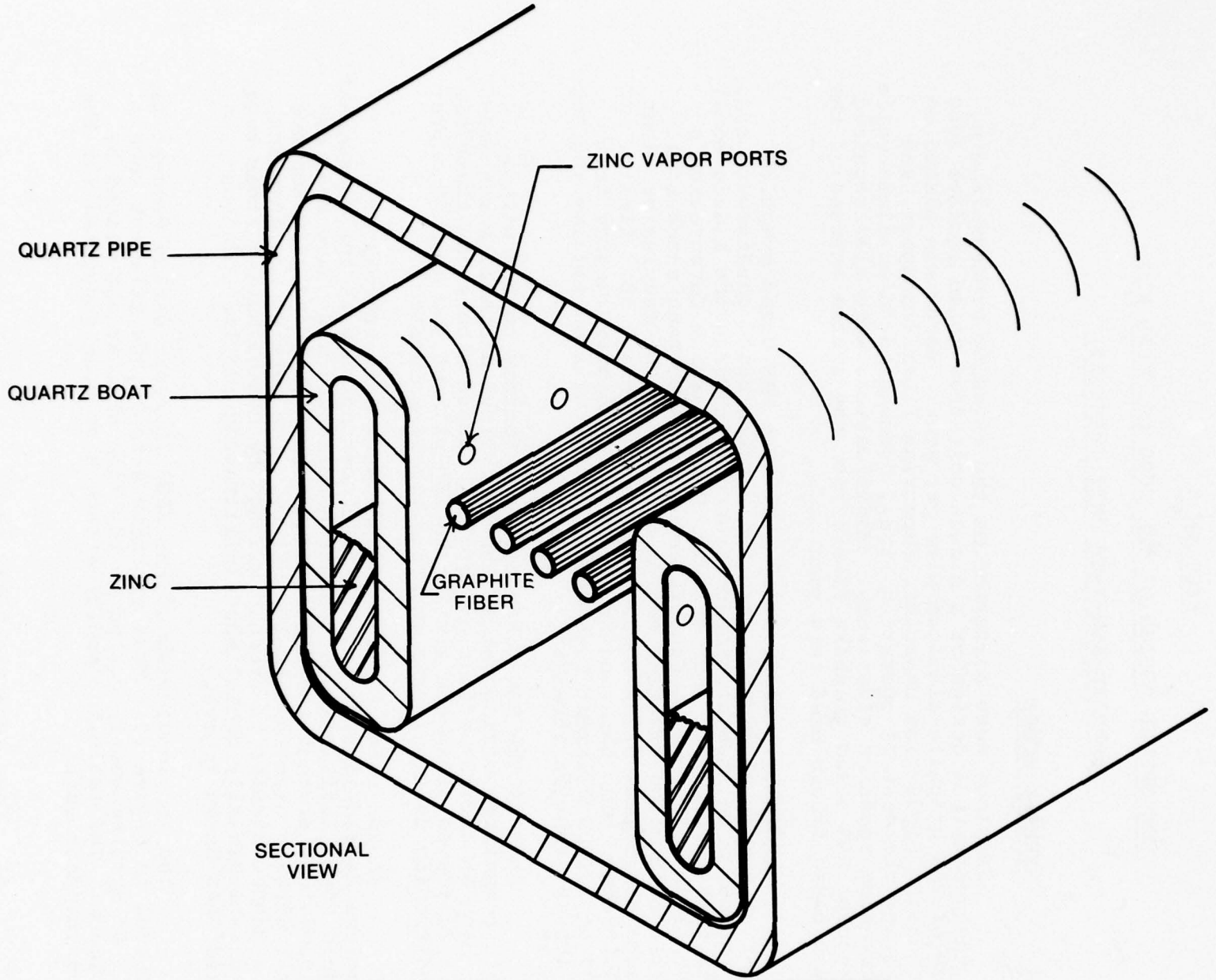


FIGURE 20 **2000 LB/YEAR PAN GRAPHITE-ALUMINUM UNIT CONCEPTION**

5.2 DETAILED SCOPE

5.2.1 Four Separate Fiber Tows

Past experience has demonstrated the feasibility of coating and wetting separate fiber tows simultaneously through the same unit. Advantages of this method include:

(1) Ability to infiltrate different fibers and tows at one time;

(2) Ability to consolidate any or all of the separate tows into one wire;

(3) Efficiency of operation and maximum utilization of reactants;

(4) Ability to switch to a strip or tape formation in future programs.

5.2.2 Square or Rectangular Zinc Sources

By utilizing a square or rectangular zinc source, the surface area of the molten zinc will remain constant during operation (and depletion). A method for continually filling the zinc container has also been included.

5.2.3 Rectangular Shaped Reaction Chamber

A square or rectangular quartz reaction chamber could solve both fiber coating and transport problems. For example, the geometry would allow zinc boats to be positioned along the side walls rather than at the chamber bottom. This would give the fiber tows more room to sag in the chamber without rubbing on stationary parts. It would also free the bottom of the chamber for fiber threading and internal exhaust clean-out systems to be designed and used.

Fiber feed-in from the air, similar to the system used on the 1000 lb./year unit, will be utilized on the 2000 lb./year process as will the open melt setup. A wire collection device will be needed to draw each graphite reinforced wire through the melt separately. This would allow the independent speed adjustment of, for example, different sized tows through the system.

SECTION 6

WIRE PRODUCTION (TASK III)

6.1 GENERAL SCOPE

Task III was devoted to the production of 100 lbs. of A201 aluminum alloy T50 graphite wire by continuous processing commensurate with a 50% yield factor. Production material was obtained in usable lengths from one to eight feet. Preliminary studies indicated that production speeds of 18" per minute to 96" per minute were possible. However, prolonged operation at the higher speeds did not produce efficient yields of wire (i.e., the scrap rate was in excess of 50%). After several weeks of optimizing during the last reporting period, it was decided to make the demonstration wire at five to six feet per minute. Empirically, this combination of flows, temperatures, and speed produced the highest net yield ever experienced.

6.2 DETAILED SCOPE

6.2.1 Transport System

Prolonged running (eight hour periods) tended to magnify minor problems with the yarn transport system at critical points such as pulleys and window boxes (i.e., places where the yarn makes a significant directional change). Experience plus independent laboratory evaluation has revealed that, while most of the T50 yarns are fairly uniform in properties, PVA coating, and splices, there are production lots which vary significantly from desired specifications. Occasionally, such a lot may be inadvertently used in wire making. The effects of such lots are manifest in excess fuzzing around pulleys and breakage of the yarns while being unrolled on the yarn creel collimator and, if enough such yarns make up the eight strand tow, wire strength values will be lower than desired. Considerable care has been taken to avoid these problems. Additionally, it is a standard practice to sample wire at several intervals during a given production period to assure its linear density and its tensile properties. Commonly, three samples are tested from a given four foot length of wire. Should any test be judged bad or the strength variation be excessive, the test is repeated. Both Nevada Engineering & Technical Corporation and Fiber Materials, Inc. tested sample production lots of wire. Some of NETCO's results are included in Table 13. NETCO has also tested many lots of yarns prior to their use in wire making to assure the best quality starting materials.

6.2.2 Gas Trap

Several conversations with both Aerospace personnel and FMI personnel prompted the substitution of an argon trap for the

Specimen ID MCI	NETCO	Linear Wt. ($x10^{-3}$ g/cm)	Breaking Load (lbs)	UTS (ksi)
3-123	1	25.0	169	112.7
3-123	2	25.3	164	105.8
3-123	3	23.9	172	118.8
4-123	4	24.8	181	120.7
4-123	5	26.4	169	105.0
4-123	6	24.6	175	116.7
4-123	7	23.8	176	121.8
5-122	8	23.2	171	118.4
5-122	9	23.9	176	121.9
5-122	10	24.2	167	115.6
5-122	11	22.4	164	118.0
5-122	12	23.8	175	121.5
4-122	13	24.5	162	108.1
4-122	14	23.9	164	113.6
4-122	15	23.3	175	121.2
4-122	16	23.2	170	117.7

TABLE 13 RESULTS OF TENSILE TESTS ON MAN TECH T50/A201 WIRE

mercury trap situated between the precoat furnace and the CVD furnace. The main problem was concern over the inadvertent transport of mercury into the CVD chamber. Experts in the area of chemical reaction kinetics have assured us that the presence of mercury, if any, should not interfere with the CVD reaction. Indeed, no evidence has been found to date that there is any problem in utilizing the mercury trap. In the interest of simplifying the system and of possibly removing an area of doubt, we ran the system with an argon trap for several weeks. No noticeable difference could be detected between the product produced with the mercury trap and the product produced without the trap. As the system occasionally evidenced oxygen asperation during shutdown cycles between runs, we decided to return to the use of the mercury trap for the remainder of the production demonstration.

We do believe, however, that the elimination of the mercury trap is desirable and will function safely if the unit is run with counter-current reaction gas flows. This reduces the likelihood of oxygen asperation as experienced with the co-current reaction gas/argon trap combination.

6.2.3 Physical Appearance

Considerable experience was obtained with balancing the tension, cooling air, argon flows, and yarn speeds to produce wire with a near round shape and good surface appearance. Generally, it is not desirable to maintain high tension on the individual yarn spools during operation. This high tension promotes breaks, pulley clogging and excessive stress on the drive mechanism. The cooling air must be turned to a low flow. Excessive cooling air causes solidification of liquid aluminum in the foot assembly which can result in yarn breakage and loss of string-up through the furnace. The argon flow in the exit tube must be adequate enough to maintain a "blanket" within the tube, thereby displacing any residual oxygen. Should oxygen be present in the exit tube during wire production, the wire shape would be flat and contorted. Finally, for a given speed, it is possible to optimize the tension, cooling and argon flows to obtain good wire.

6.2.4 Aluminum Melt

To maintain constant conditions during production runs, the aluminum level around the foot assembly and exit tube becomes critical. Significant lowering of the aluminum level during a run could result in internal solidification and clogging. Such clogging causes yarn fuzzing and possibly yarn breakage. Several methods were successfully utilized during the production phase as follows:

(1) The crucible was raised as the aluminum level decreased;

(2) Small charges of aluminum ingots were added at frequent intervals;

(3) Liquid aluminum was charged at two hour intervals.

Raising the crucible was the easiest method but produced different thermal conditions as the foot assembly was, in effect, deeper into the pot furnace. Thus, some re-balancing needed to be done each time the crucible was raised. The small charges worked well. The danger with this method would be the tendency of personnel to overcharge at any given time, thereby lowering the melt temperature and causing possible freeze-up of the melt. (Melt temperature is operated close to solidification temperatures to minimize reaction with the coated yarns.) The liquid metal charging works well but is dangerous and inconvenient. Future studies might borrow a technique from the aluminum industry whereby a "holding tank" is constantly charged and connected to the "use crucible" where the charge is being utilized. This essentially maintains a constant liquid level at a constant temperature where it is required.

SECTION 7

PROCESS SPECIFICATION FOR MANUFACTURE OF METAL MATRIX COMPOSITES

WS 18715

7.1 SCOPE

This specification provides the technical information necessary for the assembly, operation, and maintenance of a manufacturing system for the production of one thousand pounds per year of graphite-aluminum composite wire.

7.2 APPLICABLE DOCUMENTS

7.2.1 Government Documents

The following documents of the exact issue shown form a part of this specification to the extent specified herein. In the event of conflict between the documents referenced herein and the contents of this specification, the contents of this specification shall be considered a superseding requirement.

SPECIFICATIONS:

Federal

QQ-A-361	Aluminum Alloy

Military

MIL-Y-83371	High modulus graphite fiber
MIL-M-191B	Mercury

DRAWINGS:

NAVORD 3269656	1000 pounds per year graphite-aluminum unit assembly

OTHER PUBLICATIONS:

NAVSEA 0900-080-0010	Handbook of Test Methods for Evaluation and Qualification of Aluminum-Graphite Composite Materials, Section 1, Parts A & B

7.2.2 Non-Government Documents

The following documents of the exact issue shown form a part of this specification to the extent specified herein. In the event of conflict between the documents referenced herein and the contents of this specification, the contents of this specification shall be considered a superseding requirement.

SPECIFICATIONS:

ASTM Specification B 299-74	Titanium Sponge
ASTM Specification B 6-46	Zinc

Technical society and technical association specifications and standards are generally available for reference from libraries. They are also distributed among technical groups and using Federal agencies.

7.3 REQUIREMENTS

7.3.1 Equipment

The following descriptions are for use in conjunction with NAVORD drawing 3269656.

7.3.1.1 Spool Assembly

The spool assembly is the mechanism by which several strands of graphite fiber are uniformly tensioned and collimated.

7.3.1.2 Burn-Off Furnace

The burn-off furnace is a single zone furnace used for the vaporization of sizing material from the graphite fibers. It shall be capable of continuous operation at 662^{o}F (degrees Fahrenheit).

7.3.1.3 Precoat Furnace

The precoat furnace is a single zone furnace with a flowing atmosphere of hydrogen, boron trichloride, and argon used to chemically clean the surface of the graphite fibers. It shall be capable of continuous operation at 662^{o}F.

7.3.1.4 Mercury Trap Assembly

The mercury trap provides separation of the precoat furnace atmosphere from the CVD (chemical vapor deposition) furnace atmosphere.

7.3.1.5 CVD Furnace

The CVD furnace is a three zone furnace which provides the elevated temperatures required for the chemical reactions involved in the CVD process to occur. The furnace shall be capable of continuous operation at 1337°F.

7.3.1.6 CVD Reaction Tube

The CVD reaction tube provides containment for the chemical atmosphere used in the CVD process within the CVD furnace.

7.3.1.7 End Cap Assembly

The end cap assemblies provide closure for the ends of the CVD reaction tube and provide sealed openings for the passage of reactant materials into and out of the CVD reaction tube. To maintain the integrity of the seals to the CVD reaction tube, the end caps shall be water cooled to a maximum temperature of 392 F.

7.3.1.8 Zinc Boat Tube

The zinc boat is a vessel which serves as containment for liquid zinc within the CVD reaction tube.

7.3.1.9 Gas Mixing Manifold

The gas mixing manifold meters the reactant gas mixtures as required. It shall be capable of evacuation and maintaining a vacuum of 0.00193 p.s.i.a. (pounds per square inch absolute).

7.3.1.10 Exhaust System

The exhaust system provides for the removal of used reactant materials from the burn-off, precoat, and CVD processes.

7.3.1.11 Open Melt Assembly

The open melt assembly provides support and alignment for the components inserted into the liquid metal bath.

7.3.2 Materials

7.3.2.1 High modulus graphite yarn conforming to MIL-Y-83371, Type 50, Grade 1, shall be used as the fiber matrix of the aluminum matrix.

7.3.2.2 Aluminum conforming to the Federal Specification QQA-361 shall be used as the metal matrix.

7.3.2.3 Zinc for use in the zinc boat shall conform to ASTM Specification B 6-46, Grade 1 or 1a.

7.3.2.4 Titanium sponge shall conform to ASTM Specification B 299-74, Grade SL-120.

7.3.2.5 Graphite adhesive shall be Dylon Grade GC or equivalent.

7.3.2.6 Gaseous argon of 99.998% purity shall be available for delivery to the process at volumetric flow rates of 1.4 SCFM (standard cubic feet per minute). Maximum allowable impurities are as follows:

Oxygen	5PPM (parts per million)
Hydrogen	0PPM
Nitrogen	7PPM
Carbon dioxide	1PPM
Hydrocarbons	1PPM

7.3.2.7 Titanium tetrachloride liquid shall be available in minimum quantities of one quart. Typical analysis shall be as follows:

Titanium tetrachloride	99% minimum
Total other impurities including hydrochloric acid, phosgene, carbon disulfide, hydrocarbons, and titanyl chloride	1% or less

7.3.2.8 Gaseous boron trichloride of 99.9% purity shall be available for delivery to the process at volumetric flow rates of 0.00079 SCFM. Maximum allowable impurities expressed in weight percent are as follows:

Chlorine	0.05
Silicon	0.003
Sulfur dichloride	0.03
Phosgene	0.10

7.3.2.9 Gaseous hydrogen of 99.95% purity shall be available for delivery to the system at volumetric flow rates of 0.008 SCFM. Oxygen contamination shall be no greater than 20 PPM and the dew point shall be less than -75^{o}F.

7.3.2.10 Mercury for use in the gas trap shall conform to MIL-M-191B.

7.3.3 <u>Required Procedures and Operations</u>

7.3.3.1 Preassembly Notes

7.3.3.1.1 Gas Lines

All lines carrying reactant and carrier gases shall be clean and dry. They shall be evacuated to a pressure of 0.00193 p.s.i.a. or less, backfilled with argon, and maintained at a positive pressure.

7.3.3.1.2 Preparation of Gas Manifold

The gas manifold shall be disconnected from its source of reactant gases and evacuated to a pressure of 0.00193 p.s.i.a. or less. It shall then be backfilled with argon to maintain a positive pressure within the manifold.

7.3.3.1.3 Alignment

The various subsystems shall be so arranged that the path of the graphite yarn is vertically coplanar.

7.3.3.1.4 Aluminum Melt

Sufficient aluminum shall be melted to allow immersion of the open melt assembly to a depth of six inches. This aluminum shall be maintained at a temperature of 1238^{o}F plus or minus 18^{o}F.

7.3.3.2 Pre-Evacuation Assembly of CVD Unit

7.3.3.2.1 Zinc Boat Preparation

The zinc boat shall be charged with approximately 5.5 pounds of zinc. The end plug shall then be inserted and sealed with graphite cement.

7.3.3.2.2 CVD Reaction Tube

The CVD reaction tube shall be clean and dry and positioned in the CVD furnace.

7.3.3.2.3 Other Components

The open melt assembly, end caps, window boxes and their associated connecting tubing shall be clean and dry.

7.3.3.2.4 The zinc boat shall be inserted in the CVD reaction tube with its holes oriented vertically and directly below the anticipated path of the graphite yarn.

7.3.3.2.5 Approximately 0.33 pounds of titanium sponge shall be placed in the CVD reaction tube immediately downstream from the zinc boat.

7.3.3.2.6 Closure of the CVD reaction tube shall be accomplished by the installation of the end cap assemblies. Special care must

be taken to insure that the line supplying argon to the zinc boat is indeed in the hole in the end of the zinc boat, and that the holes in the zinc boat lid will direct zinc vapor toward the path of the graphite yarn.

7.3.3.2.7 Graphite yarn shall be threaded through the CVD reaction tube. Enough excess shall be left on both ends to allow assembly of the number two and three window boxes and the tubing connecting them to the CVD reaction tube.

7.3.3.2.8 Assemble the number two and three window boxes to the end cap assemblies on the CVD reaction tube with the appropriate tubing.

7.3.3.2.9 Attach the purge lines to the number two and three window boxes and install their covers.

7.3.3.2.10 Attach the argon line to the zinc boat and insert the CVD gas line into the end cap at the entrance to the CVD reaction tube.

7.3.3.2.11 Plug the open ports in the number two and three window boxes.

7.3.3.2.12 Check all tube fittings for tightness; hand tightening is adequate.

7.3.3.2.13 Evacuate the CVD system through the CVD exhaust port to a pressure of 0.00386 p.s.i.a. or less.

7.3.3.3 Post Evacuation Assembly

7.3.3.3.1 Backfill the CVD reaction tube with argon through the zinc boat line and maintain the system at a positive pressure.

7.3.3.3.2 Attach the water cooling lines to the CVD reaction tube end caps.

7.3.3.3.3 Eight spools of graphite yarn shall be placed on the spool assembly and each spool adjusted to a breakaway tension of approximately 0.011 pounds.

7.3.3.3.4 The eight strand bundle shall be pulled off the spool assembly and threaded through the burn-off and precoat furnaces and through the mercury trap. This fiber bundle shall now be attached to the yarn in the CVD reaction tube by bonding with graphite cement and the splice pulled through the system past the third window box.

7.3.3.3.5 The graphite yarn shall now be threaded through the open melt assembly and the drive roller assembly.

7.3.3.4 Start Up and Operation

7.3.3.4.1 Cooling water to the CVD reaction tube end caps shall be turned on and the flow to each cap adjusted to approximately 0.1 gallon per minute.

7.3.3.4.2 The exhaust system shall be actuated.

7.3.3.4.3 The required voltage shall be applied to all three zones of the CVD furnace and its temperature brought to approximately 800°F.

7.3.3.4.4 Upon reaching 800°F in the CVD furnace, the open melt assembly shall be immersed in the molten aluminum bath to a level approximately one inch above the top of the graphite foot. After allowing one minute for the graphite foot to warm to the melt temperature, the drive roller mechanism shall be actuated and the yarn pulled through the system at approximately 0.5 feet per minute.

7.3.3.4.5 All three zones of the CVD furnace shall be brought to 1220°F and maintained within 10°F of this temperature.

7.3.3.4.6 Apply power to the burn-off furnace and bring it to its operating temperature of 347°F and maintain it within 15°F of this temperature.

7.3.3.4.7 Apply power to the precoat furnace and bring it to its operating temperature of 662°F and maintain it within 15°F of this temperature.

7.3.3.4.8 Adjust the flows on the gas manifold to the following flow rates:

Argon carrier (Bx): 0.011 SCFM
Titanium tetrachloride/argon vapor: 0.088 SCFM
Boron trichloride vapor: 0.00039 SCFM
Argon flow to zinc boat: 0.053 SCFM
Mercury trap purge: 0.018 SCFM
No. 2 window box purge: 0.01 SCFM
Hydrogen: 0.003 SCFM
Boron trichloride to precoat: 0.00026 SCFM
Argon carrier to precoat: 0.058 SCFM
No. 3 window box purge: 0.024 SCFM
Exit tube argon: 0.024 SCFM

It should be noted that these flows are only a suggested starting point and may need to be adjusted further to achieve optimum infiltration and increased speeds through the system.

7.3.3.5 Process Shutdown

7.3.3.5.1 For temporary shutdown (periods of two hours or less) the process conditions shall be maintained as follows:

7.3.3.5.1.1 Power to the burn-off and precoat furnaces shall be discontinued.

7.3.3.5.1.2 CVD furnace temperature shall be maintained at normal process temperature.

7.3.3.5.1.3 The flow rates of gases to the process shall be as follows:

Bx: per paragraph 7.3.3.4.8
Titanium tetrachloride/argon vapor: none
Boron trichloride vapor: none
Argon to zinc boat: 0.003 SCFM
Mercury trap purge: per paragraph 7.3.3.4.8
No. 2 window box purge: 0.1 SCFM
Hydrogen: none
Boron trichloride to precoat: none
Argon carrier to precoat: none
Exit tube argon: none

7.3.3.5.2 For shutdown periods of longer than two hours, the process conditions shall be maintained as follows:

7.3.3.5.2.1 Burn-off and precoat furnaces in accordance with paragraph 7.3.3.5.1.1.

7.3.3.5.2.2 Power to the CVD furnace shall be discontinued.

7.3.3.5.2.3 Flow rates shall be those specified in paragraph 7.3.3.5.1.3.

7.3.3.6 Replacement of Open Melt Assembly Components

7.3.3.6.1 Tubing leading into and out of the liquid aluminum bath shall be replaced whenever holes or excessive alloying is noticed on the tubes.

7.3.3.6.2 Graphite components shall be replaced when broken.

7.3.3.7 System Cleanup

7.3.3.7.1 The system shall be disassembled and cleaned when any of the following conditions is in evidence.

7.3.3.7.1.1 Total time of the CVD furnace at operating temperature exceeds 120 hours.

7.3.3.7.1.2 There is evidence of lack of zinc vapor or contamination of the zinc surface in the boat.

7.3.3.7.1.3 There is oxygen, hydrogen, or other chemical contamination of the CVD process.

7.3.3.7.1.4 Contamination of the titanium sponge.

7.3.3.7.1.5 Other problems which are not apparently solvable by adjustment of flows, mechanical adjustment of the yarn transport system, or replacement of open melt assembly components.

7.3.3.7.2 Cleanup of the assembly shall be accomplished as follows:

7.3.3.7.2.1 All flows of reactant and carrier gases shall be stopped.

7.3.3.7.2.2 All furnaces shall be allowed to cool to ambient temperature.

7.3.3.7.2.3 The system shall be disassembled and thoroughly washed with water and then dried.

7.3.3.7.2.4 Reassembly shall be done in accordance with paragraphs 7.3.3.2 and 7.3.3.3 of this specification.

7.4 QUALITY ASSURANCE PROVISIONS

7.4.1 Responsibility for Inspection

Unless otherwise specified in the contract or order, the supplier is responsible for the performance of all inspection requirements as specified herein.

7.4.2 Monitoring Procedures for Equipment Used in Process

7.4.2.1 All furnace controllers shall be checked using a millivolt source to insure the levels of accuracy stated in paragraphs 7.3.3.4.5 through 7.3.3.4.7 inclusive. Checks shall be made at intervals no greater than every six months, or whenever there is cause to suspect the accuracy of a unit.

7.4.2.2 Due to the nature of the flow metering devices used in the system, recalibration is necessary only when the indicator floats are changed.

7.4.3 Monitoring Procedures for Materials

7.4.3.1 Graphite Yarn

Graphite yarn shall be tested per MIL-Y-83371.

7.4.3.2 Reactant Gases

Certificates of compliance with the appropriate specification shall be obtained for new containers of reactant gases.

7.4.3.3 Aluminum and Zinc

Certificates of compliance with the appropriate specification shall be obtained with each lot purchased.

7.4.4 Test Methods

Ninety percent rule-of-mixtures properties shall be the minimum acceptable level for the finished composite material when tested in accordance with NAVSEA 0900-080-0010, Handbook of Test Methods for Evaluation and Qualification of Aluminum-Graphite Composite Materials, Section I, Parts A and B.

7.5 NOTES

7.5.1 Intended Use

The graphite-aluminum composites fabricated under this specification will be utilized in a variety of Naval platform and weapon system applications such as skins, ribs, stiffeners, shells, ogives, and support structures.

SECTION 8

CONCLUSIONS AND RECOMMENDATIONS

The feasibility of the design and construction of a 1000 lb./year capacity graphite-aluminum unit was demonstrated during the program's production task where 100 lbs. of T50/A201 wire were produced. Wire was manufactured at speeds never before reached under continuous operation. Mechanical properties recorded were comparable to the highest values attained from past pilot plant units. The results indicate that process scale-up, including open yarn feed-in and melt methods, was successful in increasing capacity while maintaining wire integrity. Process conditions are now ready for further scale-ups to a 2000 lb./year unit and larger capacity systems for the eventual production of 100,000 to 1,000,000 pounds of material per year.

It is recommended that the following steps be taken to assure the growth of graphite-aluminum into a usable engineering structural material:

(1) Polyacrylonitrile graphite fibers be immediately incorporated into the scale-up program due to their availability and lower cost as compared to rayon based graphite;

(2) Wire production units of increased capacity be designed to accept different preforms such as continuous tapes or braided fibers;

(3) Automation of parameter control and unit operation be incorporated into the unit designs to improve process efficiency and product consistency;

(4) Quality Control standard of material, such as non-destructive testing, be developed to assure maximum product properties are attained;

(5) New graphite fibers from potential low-cost precursor materials (such as pitch) be incorporated into the program whenever the development reaches the present state-of-the-art;

(6) Fabrication techniques be developed to incorporate the composite wire into engineering parts for structural applications.

APPENDIX

METHOD OF TENSILE TESTING METAL-MATRIX WIRE COMPOSITES FOR STRENGTH AND ELASTIC MODULUS

NAVSEA Handbook 0900-080-0010

Section I, Parts A and B

SECTION I

TEST METHOD FOR WIRE

A. TENSILE TESTING METAL-MATRIX WIRE COMPOSITES FOR STRENGTH AND ELASTIC MODULUS

1. SCOPE

This method covers the determination of the tensile properties of metal-matrix composite wires reinforced by oriented, continuous, high-modulus graphite fibers.

2. SUMMARY

The tension wire specimen shown in Figure 1 is mounted in the grips of the testing machine. Load strain curves must be plotted during the test if the modulus properties are desired.

3. APPARATUS

1. Weighing scale. Suitable for weighing the wire specimen to 0.001 g.

2. Scale. Suitable for measuring the length of the wire sample to 0.01 cm.

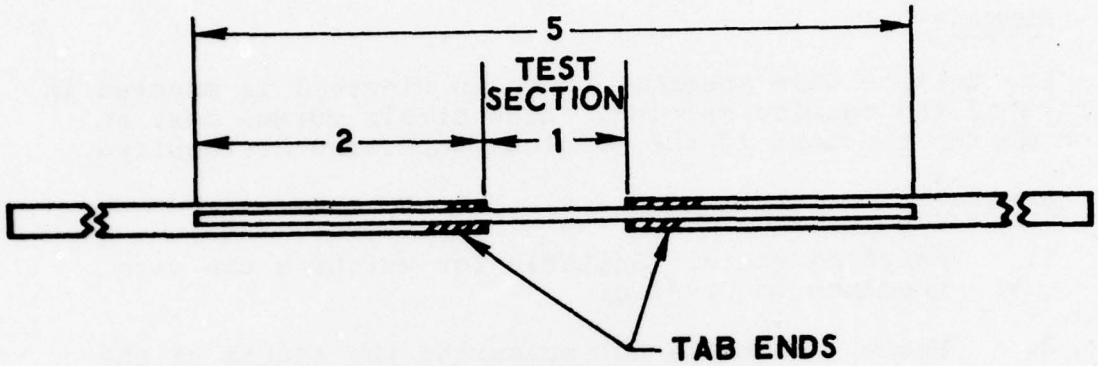
3. Testing machine. Standard Instron Universal tensile testing machine or equivalent.

4. Grips. Shall be aligned so the longitudinal axis of the specimen will coincide with the direction of applied load. The grips shall be smooth-faced or serrated with cardboard inserts to prevent tearing the nylon cord tabs attached to the specimen. Pin-type grips to which the nylon cord is tied can also be used.

5. Strain. Determined by means of a 1/2 in. mechanically attached electrical extensometer. A load versus strain record is plotted automatically.

4. TEST SPECIMEN

1. Tabs. The test specimen with tabs must be as shown in Figure 1. The tabs to be used are made of a woven nylon cord. A recommended type is Nylon Mason Line, NML 45, Type 4-1/2, manufactured by Amalgamated Cordage Corporation, Brooklyn, New York 11220. Each tab shall be long enough to grip the specimen and allow for gripping by the smooth-faced



NOTE: Diameter: ~0.062 in. Tab ends attached to composite wire with adhesive for 3/4 in. only; each tab is a minimum of 4 in. long. All dimensions are in inches.

FIGURE 1 TENSILE TEST SPECIMEN FOR COMPOSITE WIRE

machine grip or tying to a loading pin. The tabs should be gripped by the flat-faced grips ~1/16 in. above the end of the composite wire specimen.

2. Degreaser. Before attachment of the tabs, the specimen ends should be cleaned with a suitable degreaser; e.g., acetone or Freon TF degreaser. A recommended cleaner is MS-180 Freon TF degreaser manufactured by Miller-Stephenson Chemical Company, Inc., Los Angeles, California.

3. Adhesives. Any high-elongation (tough) adhesive system may be used. A recommended adhesive for coating the composite wire with 600 grit SiC is Permabond Contact Cement, manufactured by Pearl Chemical Company, Tokyo, Japan. A recommended adhesive for attaching the nylon cord to the composite wire is M Bond 200 manufactured by Micro-Measurements, Romulus, Michigan.

4. Number of test specimens. At least five specimens per 100 ft. of composite wire shall be tested. If failure of the specimen does not occur within the 1 in. test section, the test must be repeated.

5. PROCEDURE

1. Speed of testing. Shall be at a crosshead speed of 1 in./min. or 2 in./min. (strain rate of 1 in./in./min. or 2 in./in./min.). The actual strain rate of the specimen, disregarding the nylon extending, is ~0.05 in./in./min. (crosshead speed is equal to strain rate times test-section length).

2. Cross-sectional area. Determined from the linear density measurement of the test specimen. Measure the weight of the specimen to the nearest 0.001 g and the length to the nearest 0.01 cm. Calculate the linear density with the following formula and report results to three significant figures:

$$\rho_1^c = M \times L$$

where

ρ_1^c = linear density of test specimen composite (g/cm)

M = mass of the test specimen (g)

L = length of the test specimen (cm)

Use Figure 2, Composite Wire Cross-Sectional Area vs. Composite Wire Linear Density, to determine cross-sectional area. (See Section I.B.) This chart is only valid for aluminum-alloy matrix 6061 or 201 with Thornel 50 graphite in 8-ended tows. For other aluminum-alloy matrices and fiber configurations, calculations as shown in Section I.B must be made to determine the cross-sectional area.

3. Attach the tabs to the specimen as follows:

   a. Round off ends of composite wire with abrasive to prevent snagging when inserting into nylon cord.

   b. Degrease the specimen with a recommended cleaner.

   c. Apply thin coat of Permabond Contact Cement adhesive to the 2 in. specimen ends and coat with 600 grit SiC abrasive. Let adhesive dry.

   d. Insert specimen ends into the recommended nylon cord.

   e. Apply M Bond 200 adhesive catalyst to outside of nylon for 3/4 in. on either side of specimen test section. Allow to penetrate and dry for ~10 min.

4. Place the tabs in the grips of the testing machine, taking care to align the long axis of the specimen and the grips with an imaginary line joining the points of attachment of the grips to the machine. Do not grip the specimen itself, only the tabs.

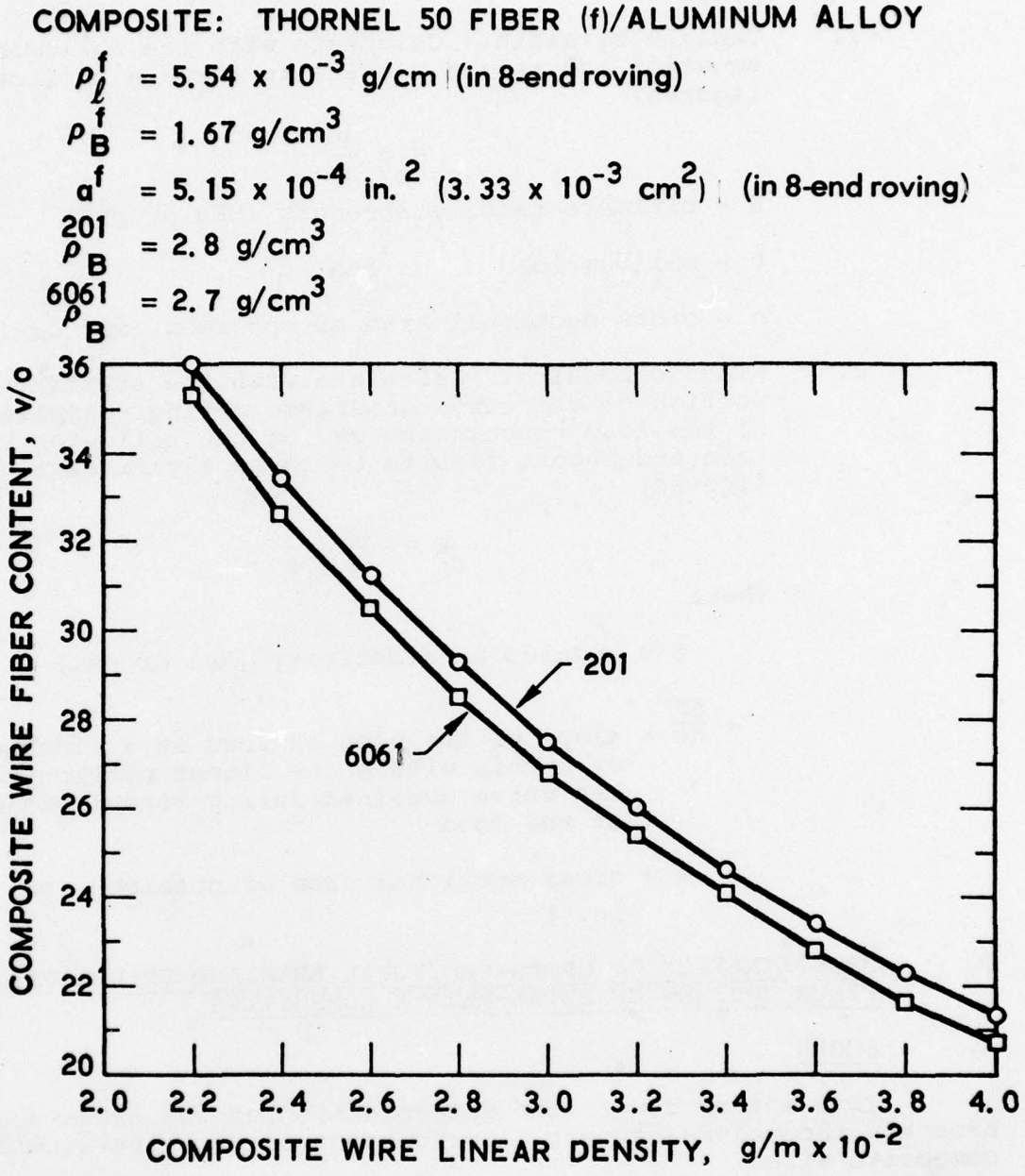
5. If strain is to be determined, attach the extensometer to the specimen.

6. Set the speed of testing to give the recommended strain rates.

7. Record load and strain continuously.

8. To determine modulus, load the specimen to 50% of expected maximum load and release to 5% of maximum load. Reapply load to maximum.

9. Record the maximum load carried by the specimen during the test.



COMPOSITE WIRE CROSS-SECTIONAL AREA ($in.^2$) VS.

FIGURE 2 COMPOSITE WIRE LINEAR DENSITY (g/m)

6. CALCULATIONS

1. Tensile strength. Calculate with the following equation and report results to three significant figures:

$$S = \frac{P}{a}$$

S = ultimate tensile strength (MPa or psi)

P = maximum load (N or lbs)

a = cross-sectional area of specimen (mm^2 or $in.^2$)

2. Elastic modulus. Calculate with the straight-line portion of the curve generated during reapplication of the load through the use of the following equation and report results to three significant figures:

$$E = \frac{\Delta P}{\Delta \varepsilon} \frac{1}{a}$$

where

E = modulus of elasticity (MPa or psi)

$\frac{\Delta P}{\Delta \varepsilon}$ = slope of the plot of load as a function of strain within the linear portion of the curve obtained during reapplication of the load

a = cross-sectional area of specimen (mm^2 or $in.^2$)

B. DETERMINATION OF CROSS-SECTIONAL ARFA AND VOLUME-PERCENT FIBER CONTENT OF METAL-MATRIX COMPOSITES

1. SCOPE

This method covers the determination of the cross-sectional area and the volume-percent fiber content of graphite-aluminum composite wire.

2. SUMMARY

A sample of graphite-aluminum composite wire is weighed and its length measured. The linear density of the sample is then determined. From the linear density of the sample, linear density of the graphite fiber, and the bulk densities of the graphite fiber and the aluminum matrix, the cross-sectional area and the volume-percent fiber content of the wire composite sample can be determined.

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METAL MATRIX COMPOSITES (GRAPHITE-ALUMINUM WIRE) PHASE I.(U)
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COMPOSITE: THORNEL 50 FIBER (f)/ALUMINUM ALLOY
(June 1974)

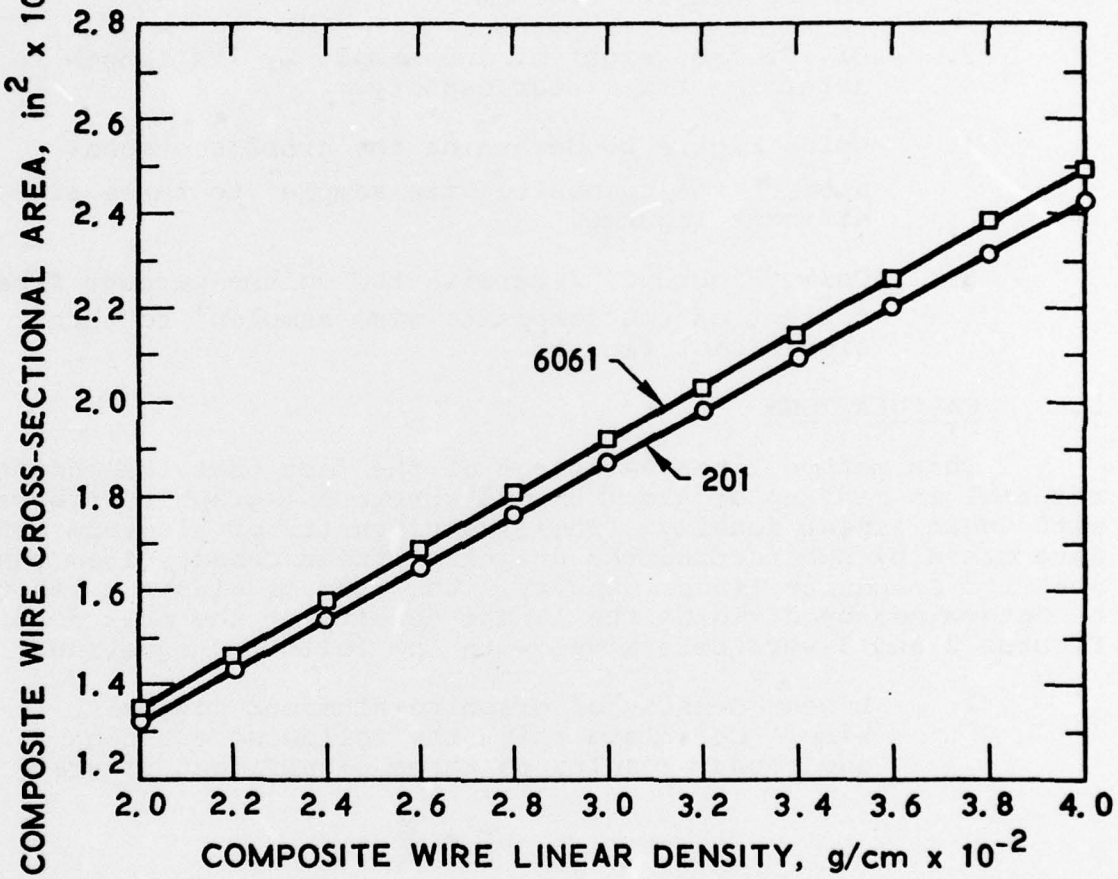
ρ_{ℓ}^{f} = 5.54 x 10^{-3} g/cm (in 8-end roving)

ρ_{B}^{f} = 1.67 g/cm^3

a^{f} = 5.15 x 10^{-4} in.^{2} (3.33 x 10^{-3} cm^2) (in 8-end roving)

ρ_{B}^{201} = 2.8 g/cm^3

ρ_{B}^{6061} = 2.7 g/cm^3



COMPOSITE WIRE FIBER CONTENT (VOLUME FRACTION) VS.

FIGURE 3 COMPOSITE WIRE LINEAR DENSITY (g/cm)

3. APPARATUS

1. Weighing scale. Suitable for weighing the wire specimen to 0.001 g.

2. Scale. Suitable for measuring the length of the wire sample to 0.01 cm.

4. PROCEDURE

1. Weigh the composite wire sample to the nearest 0.001 g.

2. Measure the length of the composite wire sample to the nearest 0.01 cm.

3. Divide the weight of the sample by its length to determine its linear density.

4. Using Figure 2, determine the cross-sectional area of the composite wire sample[1] to three significant figures.

5. Using Figure 3, determine the volume-percent fiber content of the composite wire samples[1] to three significant figures.

5. CALCULATIONS

This method takes advantage of the fact that the composite material is made up of aluminum and continuous graphite fibers with known linear density. The linear density of aluminum can be determined by subtracting the graphite linear density from the measured composite linear density. The area of aluminum can then be determined by dividing the linear density by the bulk density. Figures 2 and 3 were determined with the following equations:

1. Linear density of graphite-aluminum composite wire. Calculate using the following equation and report results to three significant figures:

$$\rho_1^c = \frac{M}{L}$$

---

[1]Figures 2 and 3 are valid only for aluminum-alloy matrices 6061 or 201 combined with 8-ended tows of Thornel 50 graphite fibers. If any other aluminum alloy or metal-matrix alloy or other graphite fiber or fiber configuration is used, then the cross-sectional area and the volume-percent fiber content must be determined with the formulas given in Section I.B.5, Calculations, above.

where

ρ_l^C = linear density of graphite-aluminum composite wire (g/cm)

M = mass of graphite-aluminum composite wire (g)

L = length of graphite-aluminum composite wire (cm)

2. Cross-sectional area of graphite-aluminum composite wire. Calculate using the following equation and report results to three significant figures:

$$a^C = a^f + a^{Al}$$

$$= \frac{\rho_l^f}{\rho_B^f} + \frac{\rho_l^c - \rho_l^f}{\rho_B^{Al}}$$

where

a^C = cross-sectional area of graphite-aluminum composite wire ($in.^2$)

a^f = cross-sectional area of 8-ended tows (strands) of Thornel 50 graphite fiber {5.15×10^{-4} $in.^2$ (3.33×10^{-3} cm^2)}

a^{Al} = cross-sectional area of the aluminum-alloy matrix ($in.^2$)

ρ_l^f = linear density of 8-ended tows (strands) of Thornel 50 graphite fiber (5.54×10^{-3} g/cm)

ρ_B^f = bulk density of Thornel 50 graphite fiber (1.67 g/cm^3)

ρ_B^{Al} = bulk density of the aluminum-alloy matrix:
aluminum alloy 6061 = 2.7 g/cm^3
aluminum alloy 201 = 2.8 g/cm^3

ρ_l^C = linear density of the graphite-aluminum composite wire (g/cm)

3. Volume-percent fiber content of graphite-aluminum composite wire. This composite consists of

continuous fibers embedded in a metal matrix; therefore, an area fraction is equivalent to a volume fraction. Calculate using the following equation and report results to three significant figures:

$$\frac{v}{o} = \frac{a^f}{a^c} (100)$$

where

$\frac{v}{o}$ = volume-percent Thornel 50 graphite fiber in the graphite-aluminum composite wire (%)

a^f = cross-sectional area of 8-ended tows (strands) of Thornel 50 graphite fiber {5.15×10^{-4} in.^{2} (3.33×10^{-3} cm^2)}

a^c = cross-sectional area of graphite-aluminum composite wire (in.^{2})

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1. Lachman, W. L. et al, Graphite Composite, U.S. Patent No. 3,860,443, 1975.

2. Lachman, W. L. et al, Graphite Composite, U.S. Patent No. 3,894,863, 1975.

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The objectives of the program were to 1) develop a production process to produce rayon precursor graphite-aluminum wire with a capacity of 1000 lbs. per year in accordance with Naval Sea Systems Command development specification for metal-matrix composites MTP-114, dated 13 January 1975, 2) optimize the process for the design of a single unit that would produce 2000 lbs. of polyacrylonitrile (PAN) graphite-aluminum wire per year, and 3) demonstrate

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20. ABSTRACT (Continued)

the 1000 lb. per year production process by producing 100 lbs. of graphite-aluminum wire.

Task I involved the design of the 1000 lb./year unit and included studies to refine techniques for operations such as open melt processing, open yarn feed-in to the Ti/B coating unit, PVA yarn sizing removal, and CVD coating.

Task II primarily consisted of optimizing the 1000 lb./year unit including system refinements and wire property testing to prepare the equipment for production capability. Data obtained from these studies were coupled with recent developments in the PAN graphite-aluminum area leading to a conceptual design of a single unit with a 2000 lb./year capacity.

Task III demonstrated the capability of the 1000 lb./year unit with the production and delivery of 100 lbs. of 201 aluminum alloy T50 graphite wire by continuous processing commensurate with a 50% yield factor. Careful system monitoring and proper mechanical testing demonstrated that the wire produced exceeded the 90% ROM requirement.